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(71) Applicant

Kansai Paint Company Limited

(Incorporated in Japan)

33-1 Kanzaki-cho, Amagasaki-shi, Hyogo-ken, Japan

(72) Inventors

Akimasa Nakahata
 Shinji Sugura
 Nobushige Numa
 Satoru Ito
 Takao Matoba
 Osamu Isozaki

(74) Agent and/or Address for Service

Withers & Rogers
 4 Dyer's Buildings, Holborn, London, EC1N 2JT,
 United Kingdom

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(54) Curable composition comprising an epoxy/silanol resin system

(57) This invention provides a curable composition comprising:

- I) a resin component containing as essential functional groups epoxy group, and silanol group and/or hydrolyzable group directly attached to silicon atom,
- II) at least one crosslinking agent selected from the group consisting of carboxylic acid compounds, polyisocyanate compounds and aminoaldehyde resins, and
- III) at least one curing catalyst selected from the group consisting of organometallic compounds, Lewis acids, protonic acids and compounds having Si-O-Al bond or bonds.

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CURABLE COMPOSITION

The present invention relates to a novel curable composition.

Known curable compositions include those comprising a hydroxyl-containing resin and a crosslinking agent such as a diisocyanate compound, a melamine resin or the like and curable with the crosslinking agent. These curable compositions, however, have drawbacks. For example, the use of diisocyanate compound gives a coating film unsatisfactory in weatherability and likely to yellow. On the other hand, the use of melamine resin usually necessitates baking at high temperatures of about 140°C or above and provides a coating film having a poor resistance to acids.

Other curable compositions are available. For example, Japanese Unexamined Patent Publication No.67553/1985 discloses a curable composition comprising an aluminum chelate compound and a vinyl polymer of alkoxy silane compound such as methacryloxypropyltrimethoxysilane. Yet the disclosed curable composition is defective. Since the silanol group formed by the hydrolysis of alkoxy silane group is the sole crosslinking functional group, the composition requires a large quantity of water for curing. Consequently large amounts

of by-products, such as alcohol, resulting from the hydrolysis give impaired properties to the cured product. Further when the composition is cured in the presence of only the moisture in air, the composition initially becomes cured at the surface, with its interior generally remaining incompletely cured, so that the curing is likely to result in a shrunk product. Further disadvantageously the curable composition forms a coating film of low adhesion to substrates and coating films.

It is an object of the present invention to provide a novel curable composition free of the above drawbacks.

It is another object of the invention to provide a novel curable composition which is excellent in curability and which gives a coating film outstanding in resistance to weather and acids, adhesion to substrates and coating films, appearance properties and the like.

These and other objects of the invention will become apparent from the following description.

According to the present invention, there is provided a curable composition comprising:

- (I) a resin component containing as essential functional groups, epoxy group, and silanol group and/or hydrolyzable group directly attached to silicon atom,
- (II) at least one crosslinking agent selected from the

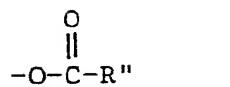
group consisting of carboxylic acid compounds, polyisocyanate compounds and aminoaldehyde resins, and (III) at least one curing catalyst selected from the group consisting of organometallic compounds, Lewis acids, protonic acids and compounds having Si-O-Al bond or bonds.

We conducted research and found that a novel curable composition comprising a resin component containing as essential functional groups silanol group and/or hydrolyzable group directly attached to silicon atom (these groups being hereinafter referred to as "silane group") and epoxy group, the above-specified crosslinking agent and the above-specified curing catalyst can overcome the foregoing drawbacks of conventional curable compositions and are excellent in curability and capable of giving a coating film outstanding in resistance to weather and acids, adhesion to substrates and coating films, appearance properties and the like. The present invention has been accomplished on the basis of this novel finding.

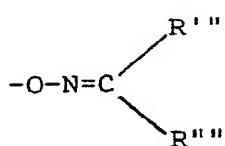
The term "hydrolyzable group directly attached to silicon atom" used herein refers to a group which hydrolyzes in the presence of water or moisture, giving silanol group. Examples of such hydrolyzable groups include those represented by the formulas

-O-R'

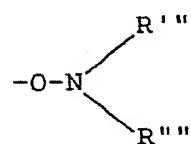
(1')



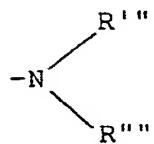
(2 ')



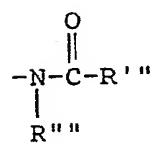
(3¹)



(4)



(5')



(6')

In the foregoing formulas, R' is an alkyl having 1 to 4 carbon atoms, R'', R''' and R'''' are the same or different and each represent an alkyl group having 1 to 8 carbon atoms, an aryl group or an aralkyl group.

Examples of the C₁₋₈ alkyl group in these formulas are methyl, ethyl, n-propyl, iso-propyl, n-butyl,

iso-butyl, sec-butyl, tert-butyl, n-pentyl, iso-pentyl, n-octyl, iso-octyl, etc. Examples of the aryl group are phenyl, toluyl, xylyl, etc. Examples of the aralkyl group are benzyl, phenethyl, etc.

Examples of the hydrolyzable group directly attached to silicon atom include a $\geqslant \text{Si}-\text{H}$ group.

The curable composition of the present invention comprising (I) the resin component, (II) the crosslinking agent and (III) the curing catalyst as described above. Among these ingredients, (I) resin component containing as essential functional groups silane group and epoxy group will be described below in detail.

Preferred examples of (I) resin component are those containing as essential functional groups silane group, epoxy group and hydroxyl group in view of a high curability.

Suitable examples of the silane group in (I) resin component are the groups of the formula (1') and (2') and silanol group which are useful to improve the curability, storage stability and the like.

Proper examples of the epoxy group in (I) resin component are alicyclic epoxy groups which rapidly react with silane group and hydroxyl group and which are useful for improvement of curability.

(I) resin component is a resin or a resin

mixture each containing silane and epoxy groups, or silane, epoxy and hydroxyl groups. Specific examples are given below in (i) to (v):

- (i) a resin containing silane and epoxy groups (hereinafter referred to as "resin component (i)");
- (ii) a resin mixture of a silane-containing resin or compound and an epoxy-containing resin or compound in which at least one of them is a resin (hereinafter referred to as "resin component (ii)");
- (iii) a resin containing silane, epoxy and hydroxyl groups (hereinafter referred to as "resin component (iii)");
- (iv) a resin mixture which is a resin component (ii) in which hydroxyl group is present in one or both of the silane-containing resin or compound and the epoxy-containing resin or compound (hereinafter referred to as "resin component (iv)"); and
- (v) a resin mixture which consists of any one of resin components (i) to (iv) and a hydroxyl-containing resin or compound (hereinafter referred to as "resin component (v)").

The resin components (i) to (v) will be described below in detail.

(i) Resin component

The resin component (i) contains at least one epoxy group and at least one silane group on the average in

the molecule and has a number-average molecular weight of about 1,000 to about 200,000, preferably about 3,000 to about 80,000. The resin component (i) having less epoxy and silane groups than the above range gives a composition lower in curability, hence undesirable. The resin component (i) having a number-average molecular weight of less than about 1,000 gives a coating film impaired in the physical properties, resistance to weather and the like, and the resin component (i) having a number-average molecular weight of above about 200,000 increases the viscosity of the composition and deteriorates the amenability of the composition to coating operation, hence undesirable.

Examples of the resin component (i) include, for example, a reaction product prepared by reacting a resin (A) having functional group, a compound (B) having epoxy group and functional group complementarily reactive with the functional group of the resin (A), and a compound (C) having silane group and functional group complementarily reactive with the functional group of the resin (A).

The resin (A), compound (B) and compound (C) are described below in detail.

The term "functional group complementarily reactive with the functional group" used herein refers to the functional groups reactive with each other. Suitable

functional groups are selectable for example from those listed below.

Table

Resin		Compound	
Kind	Functional Group	Kind	Functional Group
Resin (A)	Hydroxyl group (1)	Compound (B)	Hydroxyl group (1)
	Carboxyl group (2)		Silane group (3)
	Silane group (3)		Epoxy group (4)
	Epoxy group (4)		Isocyanato group (5)
	Isocyanato group (5)	Compound (C)	Hydroxyl group (1)
	Mercapto group (6)		Carboxyl group (2)
	Amino group (NH, NH ₂) (7)		Silane group (3)
	Acid anhydride group (8)		Epoxy group (4)
Phenolic hydroxyl group (9)			Isocyanato group (5)
Mercapto group (6)			Mercapto group (6)
Amino group (NH, NH ₂) (7)			Amino group (NH, NH ₂) (7)
Unsaturated group (8)			Unsaturated group (8)

The functional groups complementarily reactive with each other can be suitably selected from the above list to provide a combination. Suitable combinations are given below.

Combinations of functional groups of resin (A)/compound (B)

(1)/(5), (2)/(4), (3)/(3), (4)/(1), (5)/(1),
(6)/(4), (6)/(8), (7)/(4), (7)/(5), (7)/(8), (8)/(1),
(9)/(4), etc.

Combinations of functional groups of resin (A)/compound (C)

(1)/(5), (2)/(3), (2)/(4), (2)/(5), (3)/(3),
(4)/(2), (4)/(6), (4)/(7), (5)/(1), (5)/(2), (5)/(6),
(5)/(7), (6)/(4), (6)/(8), (7)/(4), (7)/(5), (7)/(8),
(8)/(1), (9)/(4), etc.

The resin (A) can be suitably selected without specific limitation from conventional resins having the foregoing functional groups. Specific examples of the resin (A) are vinyl resins, fluorine-containing resins, polyester resins, alkyd resins, silicone resins, urethane resins, polyether resins, etc.

The resin (A) has at least one functional group reactive with the functional group of the compound (B) and at least one functional group reactive with the functional group of the compound (C) on the average in the

molecule. The functional groups in the resin (A) may be the same or different.

When the resin (A) has the same functional groups, for example the resin (A) containing at least two hydroxyl groups (1) on the average may be reacted with the compound (B) containing the isocyanato group (5) and the compound (C) containing the isocyanato group (5), or the resin (A) containing at least two isocyanato groups (5) on the average may be reacted with the compound (B) containing the hydroxyl group (1) and the compound (C) containing the hydroxyl group (1).

When the resin (A) has different functional groups, for example the resin (A) containing at least one hydroxyl group (1) and at least one carboxyl group (2) on the average may be reacted with the compound (C) containing the isocyanato group (5) and the compound (B) containing the epoxy group (4).

The functional group of the compound (B) to be reacted with the functional group of the resin (A) may be epoxy. And the functional group of the compound (C) to be reacted with the functional group of the compound (A) may be silane.

Described below are the resins (A) containing hydroxyl, carboxyl, isocyanato, silane, epoxy, mercapto, amino, acid anhydride, phenolic hydroxyl or like

functional groups.

[Hydroxyl-containing resin]

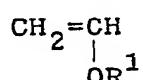
Examples of such resin include those given below in (1) to (6).

(1) Hydroxyl-containing vinyl-type resin

The resin is a copolymer of a hydroxyl-containing polymerizable unsaturated monomer (a) to be described below and when required another polymerizable unsaturated monomer (b).

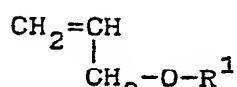
Hydroxyl-containing polymerizable unsaturated monomer (a)

Typical of such monomer are the compounds represented by the formulas (1) to (4)



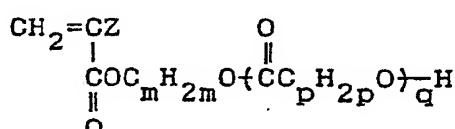
(1)

wherein R^1 is a hydrogen atom or a hydroxyalkyl group;



(2)

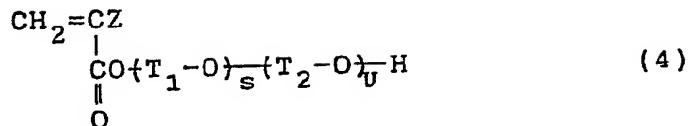
wherein R^1 is as defined above;



(3)

wherein Z is a hydrogen atom or a methyl group, m is an integer of 2 to 8, P is an integer of 2 to 18, and q is an

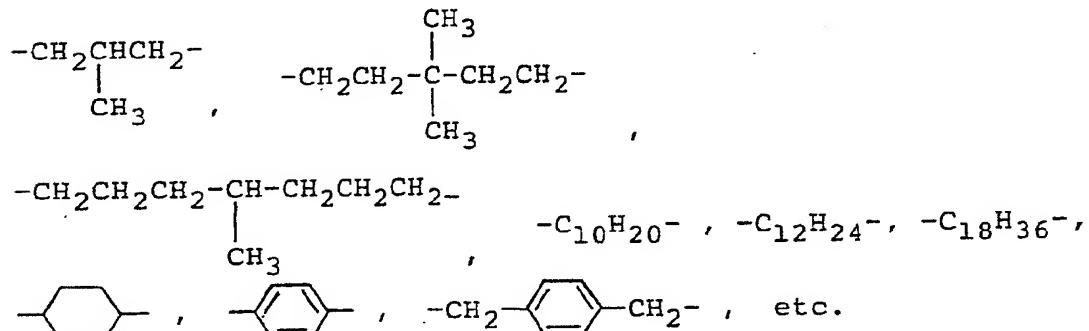
integer of 0 to 7;



wherein Z is as defined above, T_1 and T_2 are the same or different and each represent a C_{1-20} bivalent hydrocarbon group, and S and U are each an integer of 0 to 10 provided that the sum of S and U is 1 to 10.

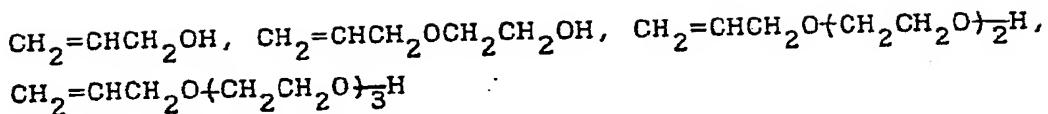
The hydroxyalkyl group in the formulas (1) and (2) has 1 to 6 carbon atoms. Specific examples are $-\text{C}_2\text{H}_4\text{OH}$, $-\text{C}_3\text{H}_6\text{OH}$, $-\text{C}_4\text{H}_8\text{OH}$, etc.

Examples of the C_{1-20} bivalent hydrocarbon group in the formula (4) are $-\text{CH}_2-$, $-\text{CH}_2-\text{CH}_2-$, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$,



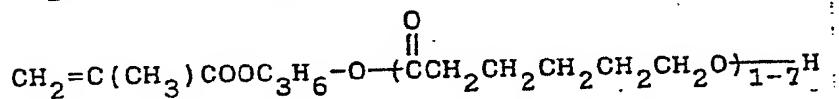
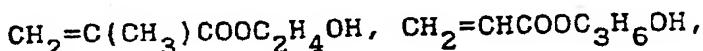
Examples of the monomer component of the formula (1) are $\text{CH}_2=\text{CHOH}$, $\text{CH}_2=\text{CHOC}_4\text{H}_8\text{OH}$, etc.

Examples of the monomer component of the formula (2) include those represented by the formulas



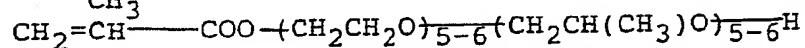
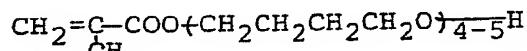
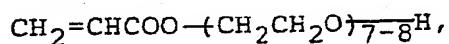
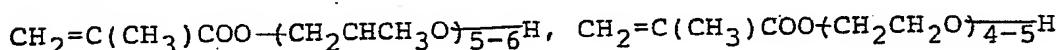
Examples of the monomer component of the formula

(3) include those represented by the formulas



Examples of the monomer component of the formula

(4) include those represented by the formulas



Also usable as the monomer (a) is an adduct of any of hydroxyl-containing unsaturated monomers of the formulas (1) to (4) with ϵ -caprolactone, γ -valerolactone or like lactone.

Polymerizable unsaturated monomer (b)

Typical of such monomer are those exemplified below in (b-1) to (b-6).

(b-1) Olefin-type compounds such as ethylene, propylene, butylene, isoprene, chloroprene, etc.

(b-2) Vinyl ethers and allyl ethers such as ethyl vinyl ether, propyl vinyl ether, isopropyl vinyl ether, butyl vinyl ether, tert-butyl vinyl ether, pentyl vinyl ether,

hexyl vinyl ether, isohexyl vinyl ether, octyl vinyl ether, 4-methyl-1-pentyl vinyl ether and like chain-like alkyl vinyl ethers, cyclopentyl vinyl ether, cyclohexyl vinyl ether and like cycloalkyl vinyl ethers, phenyl vinyl ether, o-, m- or p-tolyl vinyl ether and like aryl vinyl ethers, benzyl vinyl ether, phenethyl vinyl ether and like aralkyl vinyl ethers, etc.

(b-3) Vinyl esters and propenyl esters such as vinyl acetate, vinyl lactate, vinyl butyrate, vinyl isobutyrate, vinyl caproate, vinyl isocaproate, vinyl pivalate, vinyl caprate and like vinyl esters, isopropenyl acetate, isopropenyl propionate and like propenyl esters, etc.

(b-4) Esters of acrylic or methacrylic acids such as C₁₋₁₈ alkyl esters of acrylic or methacrylic acids including methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, butyl acrylate, hexyl acrylate, octyl acrylate, lauryl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, butyl methacrylate, hexyl methacrylate, octyl methacrylate and lauryl methacrylate; C₂₋₁₈ alkoxyalkyl esters of acrylic or methacrylic acids including methoxybutyl acrylate, methoxybutyl methacrylate, methoxyethyl acrylate, methoxyethyl methacrylate, ethoxybutyl acrylate and ethoxybutyl methacrylate, etc.

(b-5) Vinyl aromatic compounds such as styrene, α -methyl styrene, vinyltoluene, p-chlorostyrene, etc.

(b-6) Acrylonitrile, methacrylonitrile, etc.

(2) Hydroxyl- and fluorine-containing resin

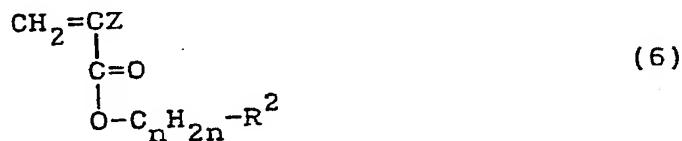
The resin is a copolymer of the hydroxyl-containing polymerizable unsaturated monomer (a), a fluorine-containing polymerizable unsaturated monomer (c) and when required the polymerizable unsaturated monomer (b).

Fluorine-containing polymerizable unsaturated monomer (c)

Typical of the monomer (c) are the compounds of the formulas (5) and (6)



wherein the groups X are the same or different and each represent a hydrogen atom, a chlorine atom, a bromine atom, a fluorine atom, an alkyl group or a haloalkyl group, provided that the compound contains at least one fluorine atom;



wherein Z is as defined above, R^2 is a fluoroalkyl group and n is an integer of 1 to 10.

The alkyl group in the formula (5) has 1 to 6

carbon atoms, preferably 1 to 4 carbon atoms. Specific examples are methyl, ethyl, propyl, isopropyl, butyl, pentyl, etc. The haloalkyl group in the formula (5) has 1 to 6 carbon atoms, preferably 1 to 4 carbon atoms. Specific examples are CF_3 , CHF_2 , CH_2F , CCl_3 , CHCl_2 , CH_2Cl , CFCl_2 , $(\text{CF}_2)_2\text{CF}_3$, $(\text{CF}_2)_3\text{CF}_3$, CF_2CH_3 , CF_2CHF_2 , CF_2Br , CH_2Br , etc.

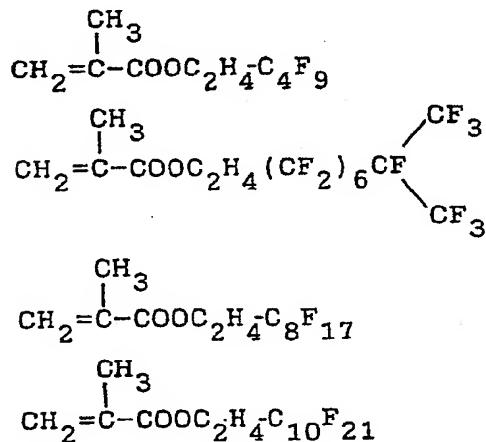
Examples of the monomer of the formula (5) include the compounds represented by the formulas

$\text{CF}_2=\text{CF}_2$, $\text{CHF}=\text{CF}_2$, $\text{CH}_2=\text{CF}_2$, $\text{CH}_2=\text{CHF}$, $\text{CClF}=\text{CF}_2$, $\text{CHCl}=\text{CF}_2$,
 $\text{CCl}_2=\text{CF}_2$, $\text{CClF}=\text{CClF}$, $\text{CHF}=\text{CCl}_2$, $\text{CH}_2=\text{CClF}$, $\text{CCl}_2=\text{CClF}$,
 $\text{CF}_3\text{CF}=\text{CF}_2$, $\text{CF}_3\text{CF}=\text{CHF}$, $\text{CF}_3\text{CH}=\text{CF}_2$, $\text{CF}_3\text{CF}=\text{CH}_2$, $\text{CHF}_2\text{CF}=\text{CHF}$,
 $\text{CH}_3\text{CF}=\text{CF}_2$, $\text{CH}_3\text{CF}=\text{CH}_2$, $\text{CF}_2\text{ClCF}=\text{CF}_2$, $\text{CF}_3\text{CCl}=\text{CF}_2$,
 $\text{CF}_3\text{CF}=\text{CFCl}$, $\text{CF}_2\text{ClCCl}=\text{CF}_2$, $\text{CF}_2\text{ClCF}=\text{CFCl}$, $\text{CFCl}_2\text{CF}=\text{CF}_2$,
 $\text{CF}_2\text{CCl}=\text{CClF}$, $\text{CF}_3\text{CCl}=\text{CCl}_2$, $\text{CClF}_2\text{CF}=\text{CCl}_2$, $\text{CCl}_3\text{CF}=\text{CF}_2$,
 $\text{CF}_2\text{ClCCl}=\text{CCl}_2$, $\text{CFCl}_2\text{CCl}=\text{CCl}_2$, $\text{CF}_3\text{CF}=\text{CHCl}$, $\text{CClF}_2\text{CF}=\text{CHCl}$,
 $\text{CF}_3\text{CCl}=\text{CHCl}$, $\text{CHF}_2\text{CCl}=\text{CCl}_2$, $\text{CF}_2\text{ClCH}=\text{CCl}_2$, $\text{CF}_2\text{ClCCl}=\text{CHCl}$,
 $\text{CCl}_3\text{CF}=\text{CHCl}$, $\text{CF}_2\text{ClCF}=\text{CF}_2$, $\text{CF}_2\text{BrCH}=\text{CF}_2$, $\text{CF}_3\text{CBr}=\text{CHBr}$,
 $\text{CF}_2\text{ClCBr}=\text{CH}_2$, $\text{CH}_2\text{BrCF}=\text{CCl}_2$, $\text{CF}_3\text{CBr}=\text{CH}_2$, $\text{CF}_2\text{CH}=\text{CHBr}$,
 $\text{CF}_2\text{BrCH}=\text{CHF}$, $\text{CF}_2\text{BrCF}=\text{CF}_2$, $\text{CF}_3\text{CF}_2\text{CF}=\text{CF}_2$, $\text{CF}_3\text{CF}=\text{CFCF}_3$,
 $\text{CF}_3\text{CH}=\text{CFCF}_3$, $\text{CF}_2=\text{CFCF}_2\text{CHF}_2$, $\text{CF}_3\text{CF}_2\text{CF}=\text{CH}_2$, $\text{CF}_3\text{CH}=\text{CHCF}_3$,
 $\text{CF}_2=\text{CFCF}_2\text{CH}_3$, $\text{CF}_2=\text{CFCH}_2\text{CH}_3$, $\text{CF}_3\text{CH}_2\text{CH}=\text{CH}_2$, $\text{CF}_3\text{CH}=\text{CHCH}_3$,
 $\text{CF}_2=\text{CHCH}_2\text{CH}_3$, $\text{CH}_3\text{CF}_2\text{CH}=\text{CH}_2$, $\text{CFH}_2\text{CH}=\text{CHCFH}_2$, $\text{CH}_3\text{CF}_2\text{CH}=\text{CH}_2$,
 $\text{CH}_2=\text{CFCH}_2\text{CH}_3$, $\text{CF}_3(\text{CF}_2)_2\text{CF}=\text{CF}_2$, $\text{CF}_3(\text{CF}_2)_3\text{CF}=\text{CF}_2$

The fluoroalkyl group in the formula (6) has 3

to 21 carbon atoms. Specific examples are C_4F_9 , $(CF_2)_6CF(CF_3)_2$, C_8F_{17} , $C_{10}F_{21}$, etc.

Examples of the monomer of the formula (6) include the compounds represented by the formulas



(3) Hydroxyl-containing polyester resin

The resin is prepared by esterification or ester interchange reaction of a polybasic acid with a polyhydric alcohol. Examples of useful polybasic acids include the compounds having 2 to 4 carboxyl groups or methyl carboxylate groups per molecule such as phthalic acid or anhydride, isophthalic acid, terephthalic acid, maleic acid or anhydride, pyromellitic acid or anhydride, trimellitic acid or anhydride, succinic acid or anhydride, sebacic acid, azelaic acid, dodecanedicarboxylic acid, dimethyl isophthalate, dimethyl terephthalate and the like. Examples of useful polyhydric alcohols are alcohols

having 2 to 6 hydroxyl groups per molecule such as ethylene glycol, polyethylene glycol, propylene glycol, neopentyl glycol, 1,6-hexanediol, trimethylolpropane, pentaerythritol, glycerin, tricyclodecanedimethanol, etc. When required, monobasic acids are usable for preparation of the resin and include fatty acids of castor oil, soybean oil, tall oil, linseed oil or the like, and benzoic acid.

(4) Hydroxyl-containing polyurethane resin

The resin is an isocyanato-free one prepared by modifying a hydroxyl-containing vinyl-type resin, a hydroxyl- and fluorine-containing resin, a hydroxyl-containing polyester resin or the like with a polyisocyanate compound such as tolylene diisocyanate, xylene diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate or the like.

(5) Hydroxyl-containing silicone resin

The resin is an alkoxy silane-free and silanol-free one prepared by modifying a hydroxyl-containing vinyl-type resin, hydroxyl- and fluorine-containing resin, hydroxyl-containing polyester resin or the like with a silicone resin such as Z-6018 or Z-6188 (trademarks for products of Dow Corning Ltd.), or SH 5050, SH 6018 or SH 6188 (trademarks for products of Toray Silicone Co., Ltd.).

(6) Reaction product prepared by hydrolysis of a portion or the whole of a polyvinyl acetate or a copolymer of vinyl acetate and another polymerizable unsaturated monomer.

[Carboxyl-containing resin]

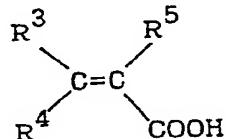
Typical examples of such resin are given below in (1) to (3):

(1) Carboxyl-containing vinyl resin.

The resin is a polymer of a carboxyl-containing polymerizable unsaturated monomer (d) and when required the polymerizable unsaturated monomer (b).

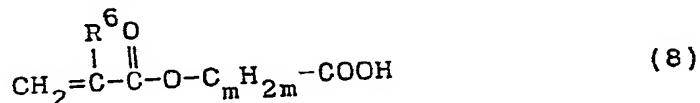
Carboxyl-containing polymerizable unsaturated monomer (d)

Typical of the monomer (d) are the compounds represented by the formulas (7) and (8)



(7)

wherein R³ is a hydrogen atom or a lower alkyl group, R⁴ is a hydrogen atom, a lower alkyl group or a carboxyl group, and R⁵ is a hydrogen atom, a lower alkyl group or a carboxy-lower alkyl group;



(8)

wherein R⁶ is a hydrogen atom or a methyl group, and m is

as defined above.

Preferred lower alkyl groups in the formula (7) are those having 1 to 4 carbon atoms, especially methyl.

Examples of the monomer of the formula (7) are acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, maleic anhydride, fumaric acid, etc.

Examples of the monomer of the formula (8) are 2-carboxyethyl acrylate or methacrylate, 2-carboxypropyl acrylate or methacrylate, 5-carboxypentyl acrylate or methacrylate, etc.

Also usable as the monomer (d) is an adduct of 1 mole of the hydroxyl-containing polymerizable unsaturated monomer (a) with 1 mole of a carboxylic anhydride compound such as maleic anhydride, itaconic anhydride, succinic anhydride, phthalic anhydride or the like.

(2) Carboxyl- and fluorine-containing resin

The resin is a copolymer of the fluorine-containing polymerizable unsaturated monomer (c), the carboxyl-containing polymerizable unsaturated monomer (d), and when required the polymerizable unsaturated monomer (b). These monomers can be any of the above-mentioned monomers.

Also usable is a resin prepared by reacting the fluorine-containing polyol resin with the carboxylic anhydride compound.

(3) Carboxyl-containing polyester resin

Examples of such resin are a resin prepared by esterification of the polybasic acid or the corresponding anhydride with the polyhydric alcohol, a resin prepared by adducting an acid anhydride to the hydroxyl-containing polyester resin, etc.

[Isocyanato-containing resin]

Examples of such resin include those given below in (1) to (4).

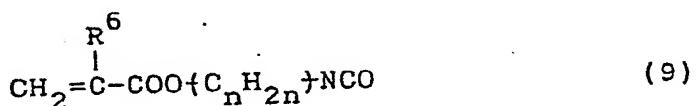
(1) Isocyanato-containing vinyl resin

The resin is a polymer of an isocyanato-containing polymerizable unsaturated monomer (e) and when required the polymerizable unsaturated monomer (b).

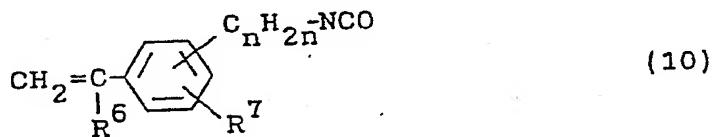
Isocyanato-containing polymerizable unsaturated monomer

(e)

Typical examples of the monomer (e) are those represented by the formulas (9) and (10)



wherein R^6 and n are as defined above, examples of the monomer of the formula (9) being isocyanate ethyl acrylate or methacrylate; and



wherein R⁶ and n are as defined above and R⁷ is a hydrogen atom or an alkyl group having 1 to 5 carbon atoms, examples of the monomer of the formula (10) being α,α -dimethyl- m -isopropenyl benzyl isocyanate.

Also usable as the monomer (e) is a reaction product of 1 mole of the hydroxyl-containing polymerizable unsaturated monomer (a) and 1 mole of a polyisocyanate compound. Examples of useful polyisocyanate compounds are tolylene diisocyanate, 1,6-hexamethylene diisocyanate, 4,4'-diphenylmethane diisocyanate, 4,4'-diphenyl ether diisocyanate, phenylene diisocyanate, naphthalene diisocyanate, biphenylene diisocyanate, 3,3'-dimethyl-4,4'-biphenylene diisocyanate, dicyclohexylmethane, 4,4'-diisocyanate, p-xylylene diisocyanate, m -xylylene diisocyanate, bis(4-isocyanatephenyl)sulfone, isopropylidenebis(4-phenylisocyanate), lysine isocyanate and isophorone diisocyanate, polymers thereof, biurets thereof, etc.

Also usable as the isocyanato-containing vinyl resin is a reaction product prepared by reacting a hydroxyl-containing vinyl-type resin with, e.g., the polyisocyanate compound.

(2) Isocyanato- and fluorine-containing resin

The resin is one prepared by reacting the hydroxyl- and fluorine-containing resin with the

polyisocyanate compound.

(3) Isocyanato-containing polyester resin

The resin is one prepared by reacting the hydroxyl-containing polyester resin with the polyisocyanate compound.

(4) Isocyanato-containing polyurethane resin

The resin is one prepared by reacting a polyether polyol with the polyisocyanate compound.

Examples of the polyether polyol are polyether polyols prepared by subjecting glycols (such as ethylene glycol, propylene glycol and the like) and alkylene oxides (such as ethylene oxide, propylene oxide and the like) to polymerization, polytetramethylene ether glycols prepared by subjecting tetrahydrofuran to cationic polymerization, etc.

[Silane-containing resin]

Examples of the resin are given below in (1) to (4).

(1) A resin prepared by reacting the hydroxyl-containing resin with an isocyanato-containing silane compound to be described later.

(2) A resin prepared by reacting the isocyanato-containing resin with a hydroxyl-containing silane compound to be described later.

(3) A silicone resin used in preparation of the hydroxyl-

containing silicone resin.

(4) A polymer of a silane-containing polymerizable unsaturated monomer (g) to be described later with when required the polymerizable unsaturated monomer (b) and the fluorine-containing polymerizable unsaturated monomer (c).
[Epoxy-containing resin]

Examples of the resin are given below in (1) and (2).

(1) A resin prepared by reacting the hydroxyl-containing resin with an isocyanato-containing epoxy compound to be described later

(2) A polymer of an epoxy-containing polymerizable unsaturated monomer (f) to be described later and when required the polymerizable unsaturated monomer (b) and the fluorine-containing polymerizable unsaturated monomer (c).
[Mercapto-containing resin]

The resin is one prepared by reacting the hydroxyl-containing resin or the silane-containing resin with a mercapto-containing compound to be described later.

[Amino-containing resin]

The resin is one prepared by reacting the hydroxyl-containing resin or the silane-containing resin with an amino-containing compound to be described later.

[Acid anhydride group-containing resin]

Examples of such resin are given below in (1)

and (2).

(1) A polymer of the monomer (d) containing acid anhydride group (such as maleic anhydride, itaconic anhydride, succinic anhydride or the like) and when required the polymerizable unsaturated monomer (b).

(2) A resin consisting essentially of an acid anhydride (such as trimellitic acid, pyromellitic anhydride or the like) and a polyhydric alcohol.

[Phenolic hydroxyl-containing resin]

Examples of the resin are given below in (1) to (4).

(1) A phenol- or cresol-type resin (such as phenol-type novolak resin, phenol-type resol resin, cresol-type novolak resin, etc.).

(2) A polymer comprising as the essential monomer component a phenolic hydroxyl-containing polymerizable monomer (such as p-vinyl phenol, etc.)

(3) A resin prepared from the epoxy-containing resin and a polyvalent phenolic compound (such as catechol, resorcin, hydroquinone, pyrogallol, hydroxyhydroquinone or the like) in such proportions that the resulting resin contains an excess amount of polyvalent phenolic compound.

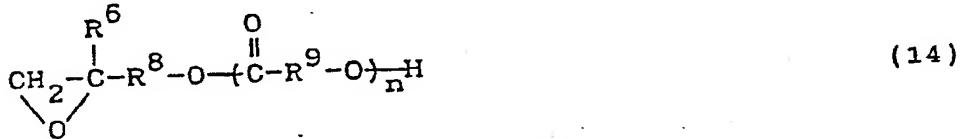
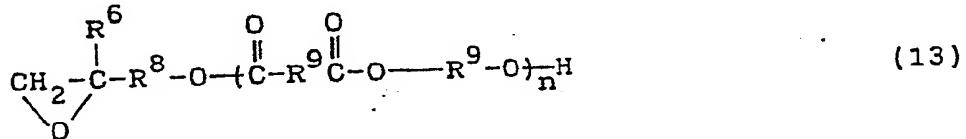
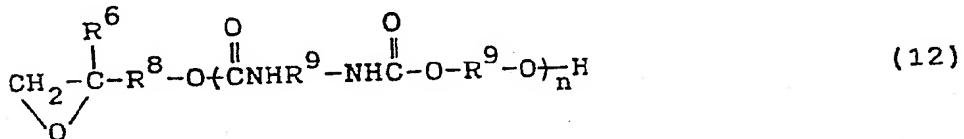
(4) A resin prepared by reacting an epoxy-containing resin with a phenolic hydroxyl-containing compound (such as hydroxybenzoic acid).

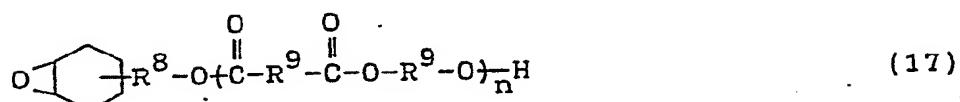
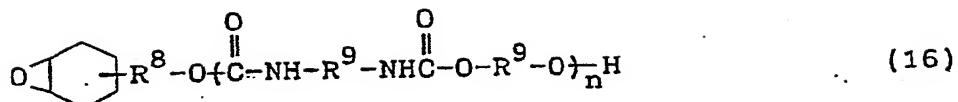
The compound (B) useful for the resin component (i) has in the molecule at least one epoxy group and at least one functional group reactive with the functional group of the resin (A). The functional group reactive with the functional group of the resin (A) may be epoxy. When the functional group is epoxy, the compound contains at least two epoxy groups in the molecule.

Described below are typical examples of the compound (B).

[Hydroxyl-containing epoxy compound]

Examples of such compound include the compounds represented by the formulas (11) to (21)

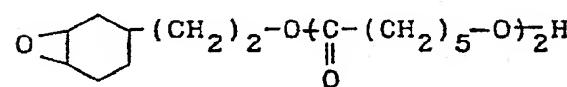
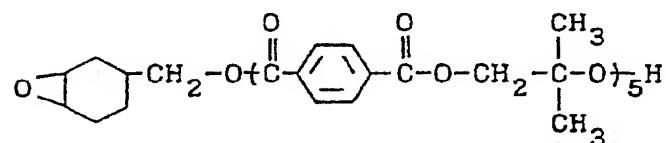
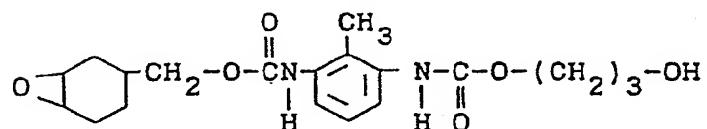
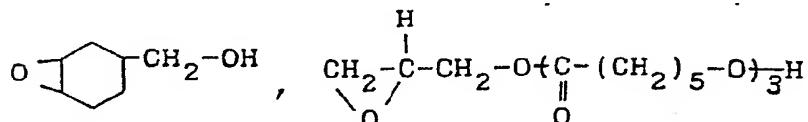
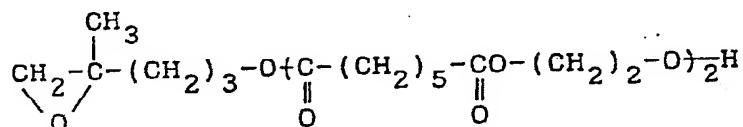
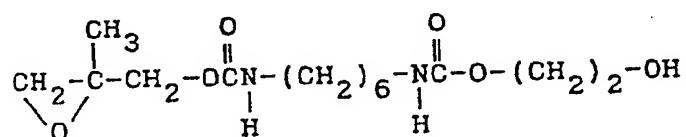
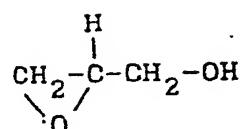


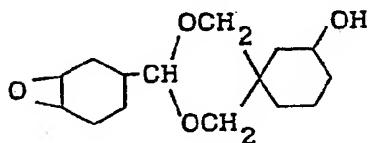
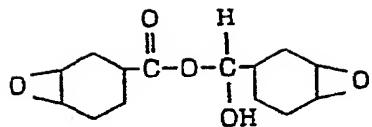


In the foregoing formulas, R^6 and n are as defined above, R^8 is a C_{1-8} bivalent hydrocarbon group and the groups R^9 are the same or different and each represent a C_{1-20} bivalent hydrocarbon group.

In the formulas (11) to (21), the C_{1-8} bivalent hydrocarbon group can be suitably selected from the foregoing C_{1-20} bivalent hydrocarbon groups, and the C_{1-20} bivalent hydrocarbon groups include the above examples of such group.

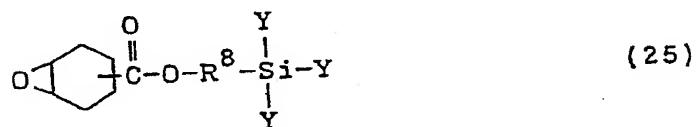
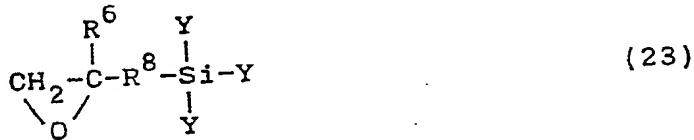
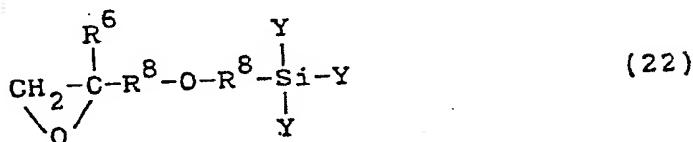
Specific examples of the compounds of the formulas (11) to (21) are those represented by the formulas





[Silane-containing epoxy compound]

Examples of such compound include the compounds represented by the formulas (22) to (25)

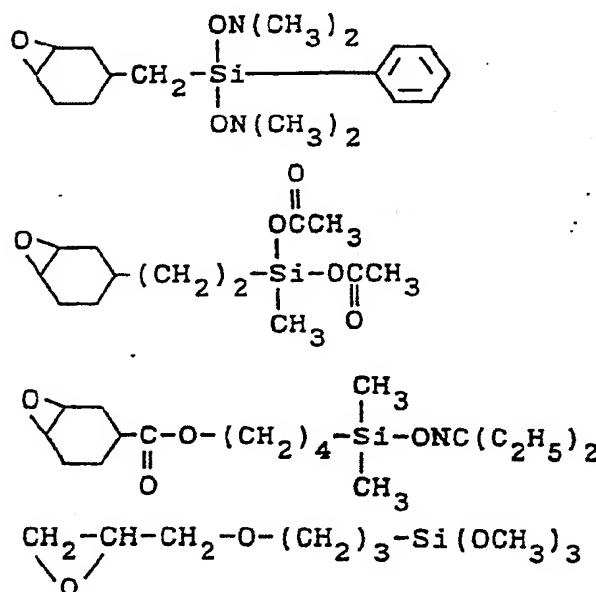


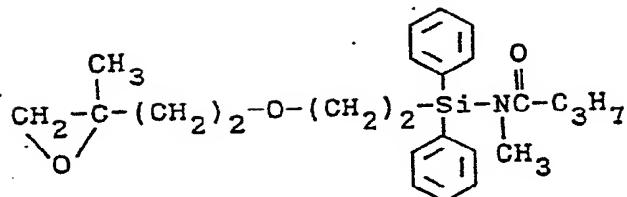
In the foregoing formulas, R^6 and R^8 have the same meaning as above, the groups R^8 are the same or

different, and the groups Y are the same or different and each represent a hydrogen atom, a hydroxyl group, a hydrolyzable group, a C₁₋₈ alkyl group, an aryl group or an aralkyl group, provided that at least one of the groups Y is a hydrogen atom, a hydroxyl group or a hydrolyzable group.

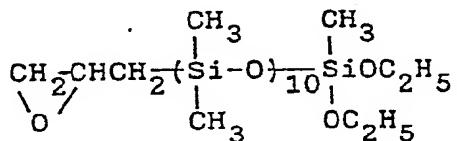
Examples of hydrolyzable groups in the formulas (22) to (25) include those of the formulas (1') to (6'). Examples of the C₁₋₈ alkyl group, aryl group and aralkyl group in the formulas (22) to (25) include the above examples of these groups.

Specific examples of the compounds of the formulas (22) to (25) are those represented by the formulas



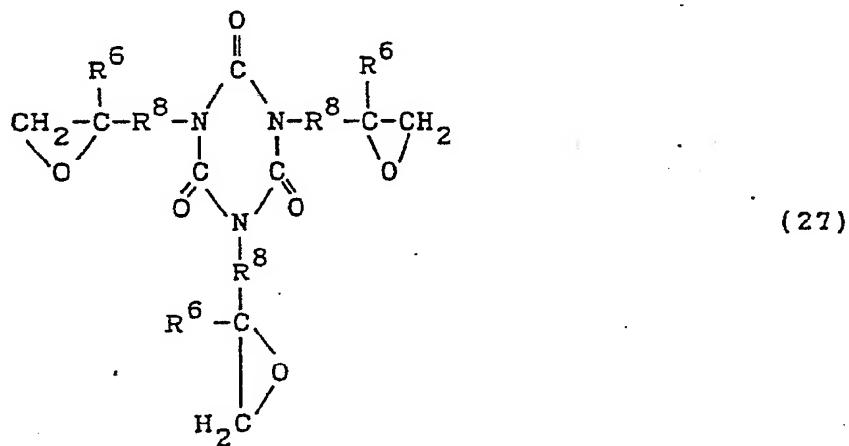
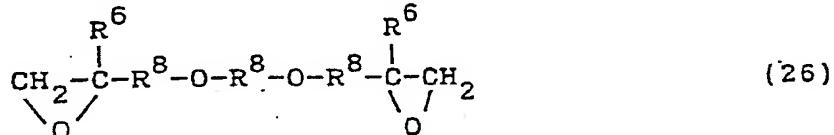


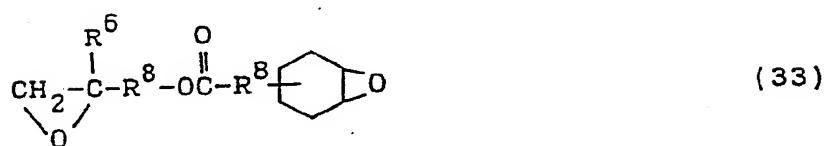
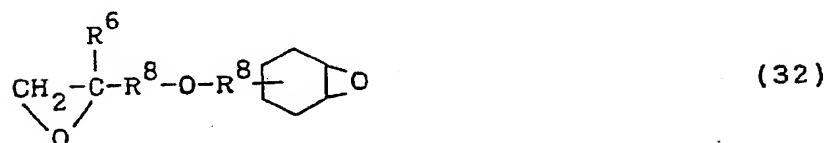
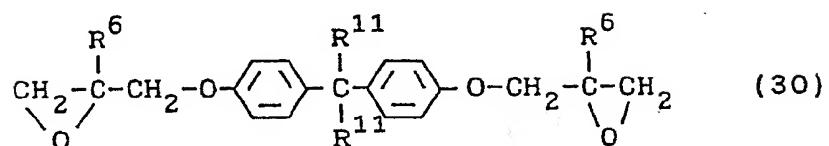
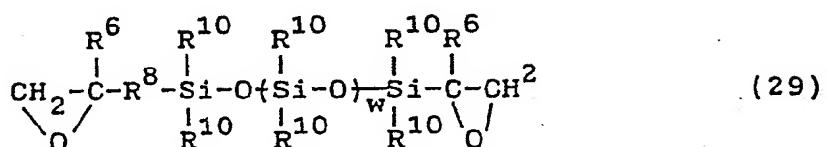
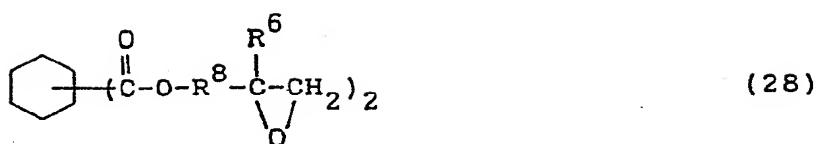
Also usable is a condensation product of each compound of the formulas (22) to (25) with a polysilane compound to be described later (such as compounds of the formulas (38) to (40)). Specific examples of such compound are those represented by the formula



[Polyepoxy compound]

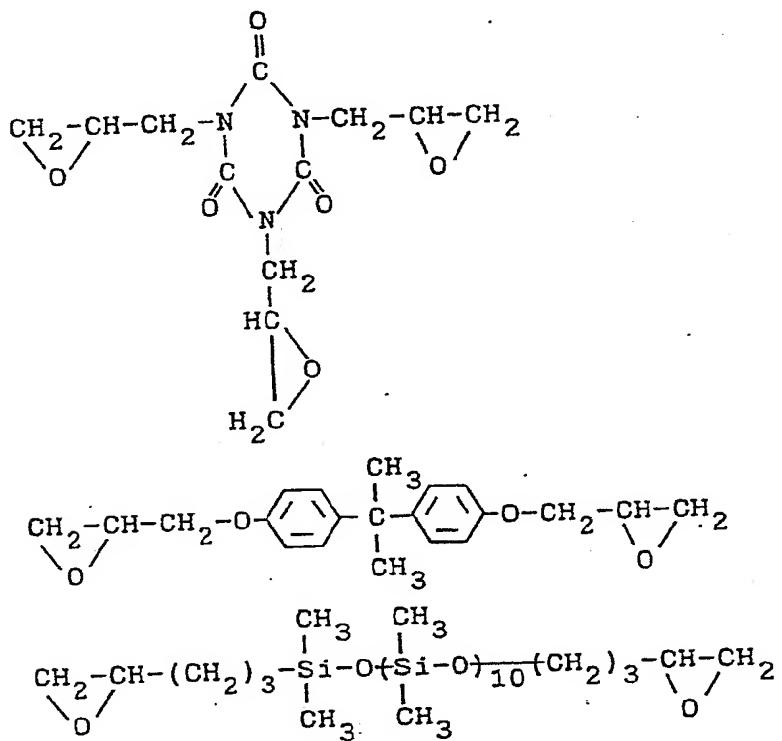
Examples of such compound include the compounds represented by the formulas (26) to (33)

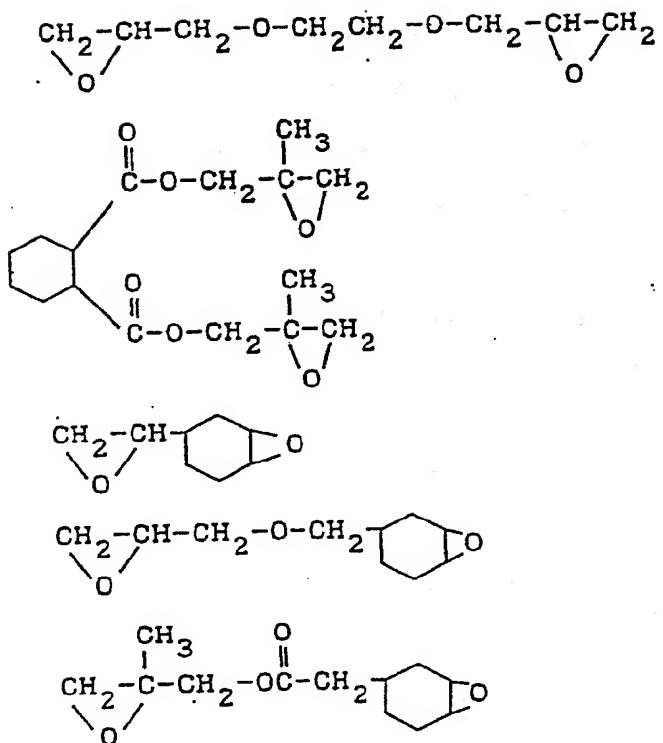




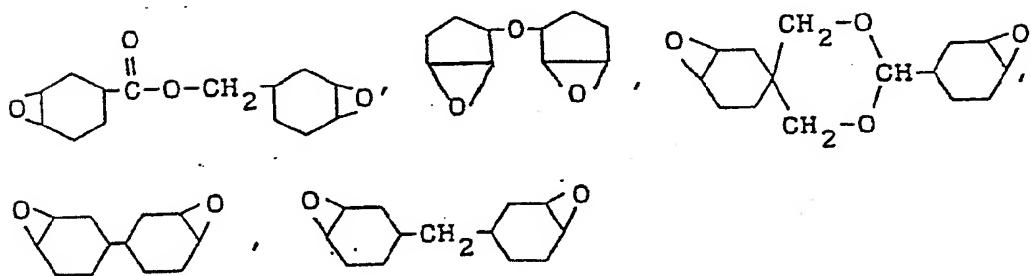
In the foregoing formulas, R^6 and R^8 are as defined above, the groups R^6 are the same or different, the R^{10} groups are the same or different and are each a C_{1-8} alkyl group, an aryl group or an aralkyl group, the groups R^{11} are the same or different and are each a hydrogen atom or a C_{1-4} alkyl group, and w is an integer of 0 to 10.

Examples of the compounds of the formulas (26) to (33) are those represented by the formulas

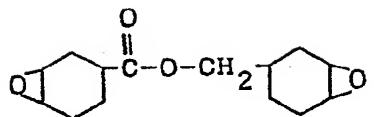


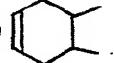


Further examples of the polyepoxy compound
include those represented by the formulas



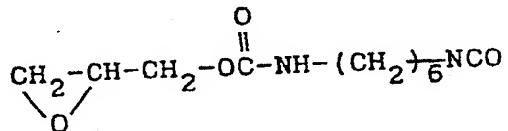
Also usable as the polyepoxy compound is an adduct of  with a polyisocyanate compound to be exemplified below. Examples of useful polyisocyanate compounds are organic diisocyanates such as hexamethylene diisocyanate, trimethyl hexamethylene diisocyanate and like aliphatic diisocyanates, hydrogenated xylylene diisocyanate, isophorone diisocyanate and like cyclic aliphatic diisocyanates, tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate and like aromatic diisocyanates; an adduct of the organic diisocyanate with a polyhydric alcohol, a low-molecular-weight polyester resin, water or the like; a copolymer of such organic diisocyanates with each other, isocyanate biurets, etc. Representative commercial products of such polyisocyanate compounds are those available under the trademarks: "BURNOCK D-750, -800, DN-950, DN-970 and -15-455" (products of Dainippon Ink And Chemicals Incorporated), "DESMODUL L, NHL, IL and N3390" (products of Bayer AG, West Germany), "TAKENATE D-102, -202, -110N and -123N" (products of Takeda Chemical Industries, Ltd.), "COLONATE-L, -HL, -EH and -203" (products of Nippon Polyurethane Kogyo K.K.), "DURANATE 24A-90CX" (product of Asahi Chemical Industry Co., Ltd.), etc. Also usable as the polyepoxy compound are an adduct of a compound of the formula



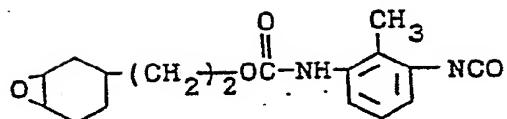
with a polybasic acid; a product prepared by oxidizing an ester having unsaturated group such as a group  in the molecule with a peracetic acid or the like, examples of the ester being an ester of 900 in number-average molecular weight prepared by esterifying tetrahydronthalic anhydride, trimethylolpropane, 1,4-butanediol or the like.

[Isocyanato-containing epoxy compound]

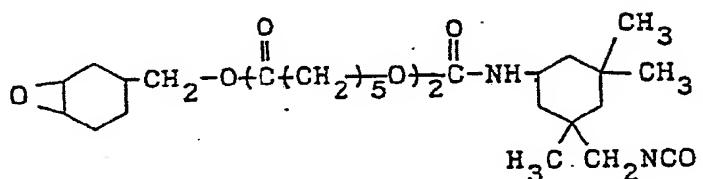
Examples of such compound include those prepared by reacting the hydroxyl-containing epoxy compound with the polyisocyanate compound such that the epoxy and isocyanato groups remain in the reaction product. Examples of such reaction product are a reaction product of the compound of the formula (11) with a hexamethylene diisocyanate



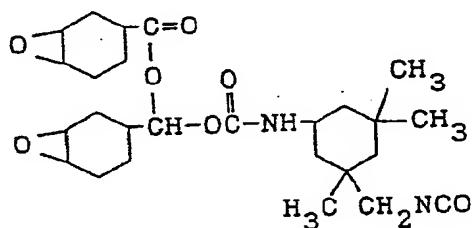
a reaction product of the compound of the formula (15) with a tolylene diisocyanate



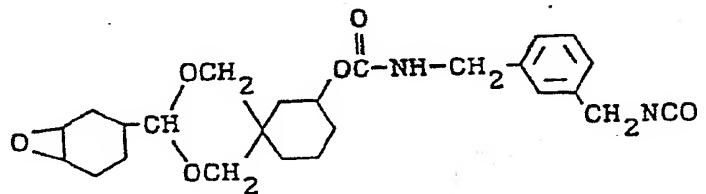
a reaction product of the compound of the formula (18)
with an isophorone diisocyanate



a reaction product of the compound of the formula (20)
with an isophorone diisocyanate



a reaction product of the compound of the formula (21)
with a xyllylene diisocyanate



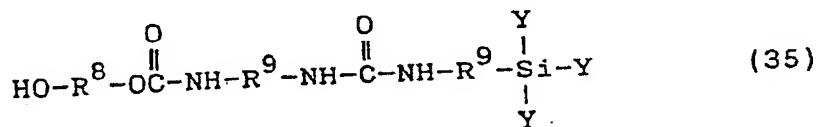
The unsaturated group-containing compound can be any of silane-containing polymerizable unsaturated monomers to be described later.

The compound (C) useful for the resin component (i) has in the molecule at least one silane group and at least one functional group reactive with the functional group of the resin (A). The functional group reactive with the functional group of the resin (A) may be silane. In this case, the compound contains at least two silane groups in the molecule.

Described below are typical examples of the compound (C).

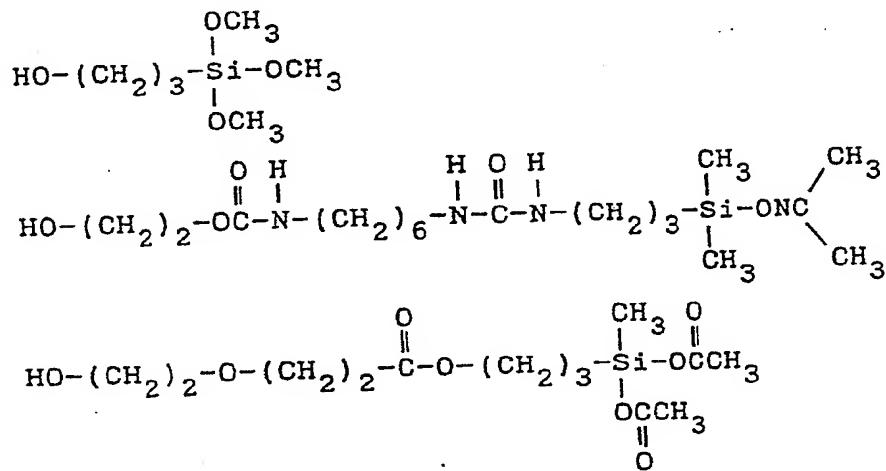
[Hydroxyl-containing silane compound]

Examples of such compound are those represented by the formulas (34) to (36)

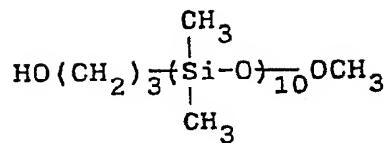


In the formulas, R⁸, R⁹ and Y are as defined above; the groups R⁸ are the same or different, the groups R⁹ are the same or different, and the groups Y are the same or different, provided that at least one of the groups Y is a hydrogen atom, a hydroxyl group or a hydrolyzable group.

Specific examples of the compounds of the formulas (34) to (36) are those represented by the formulas



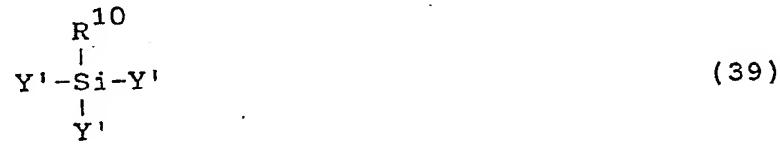
Also usable as such compound is a condensation product of each compound of the formulas (34) to (36) with a polysilane compound to be described later. Examples of such condensation product include the compound represented by the formula



[Polysilane compound]

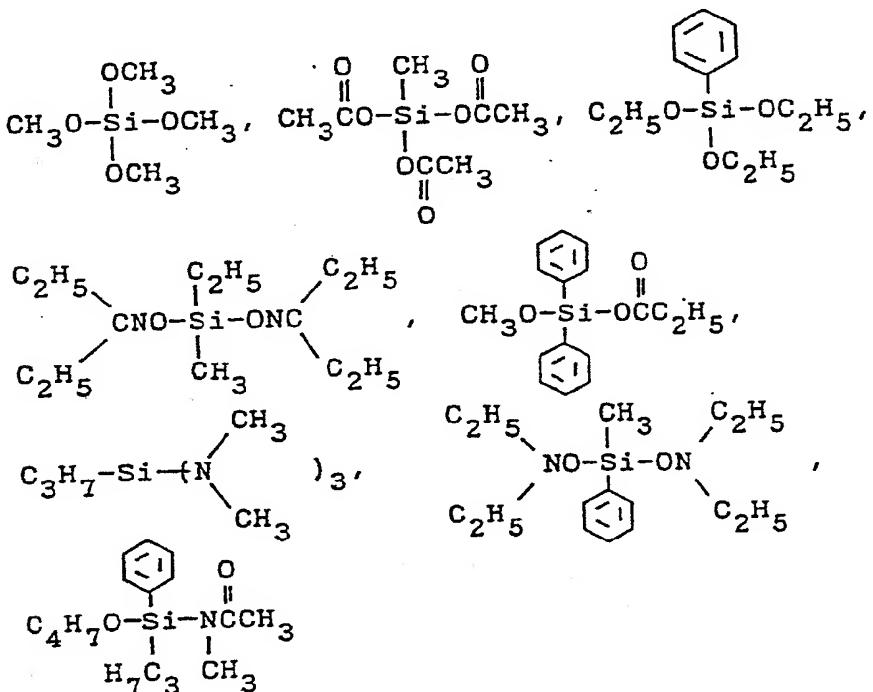
The polysilane compound contains, in the molecule, at least two groups selected from hydrolyzable groups directly attached to silicon atom and silanol group.

Examples of such compound are those represented by the formulas (38) to (40)



In the foregoing formulas, the groups Y' are the same or different and each represent a hydrogen atom, a hydroxyl group or a hydrolyzable group, R¹⁰ is as defined above and the groups R¹⁰ are the same or different.

Specific examples of the compounds having the formulas (38) to (40) are dimethyldimethoxysilane, dibutyldimethoxysilane, diisopropyldipropoxysilane, diphenyldibutoxysilane, diphenyldiethoxysilane, diethyldisilanol, dihexyldisilanol, methyltrimethoxysilane, methyltriethoxysilane, ethyltriethoxysilane, propyltrimethoxysilane, phenyltriethoxysilane, phenyltributyoxy silane, hexyltriacetoxy silane, methyltrisilanol, phenyltrisilanol, tetramethoxysilane, tetraethoxysilane, tetrapropoxysilane, tetraacetoxysilane, di-iso-propoxydivaleroxy silane, tetrasilanol, and the compounds represented by the formulas



A condensation product of such polysilane compounds with each other is also usable.

[Epoxy-containing silane compound]

Examples of such compound include the foregoing silane-containing epoxy compounds.

[Isocyanato-containing silane compound]

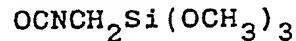
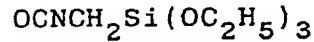
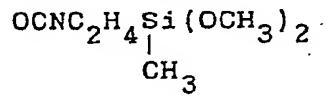
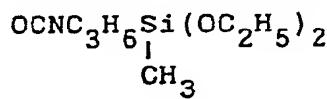
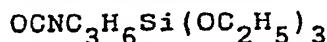
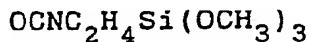
Examples of such compound include the compound represented by the formula (41)

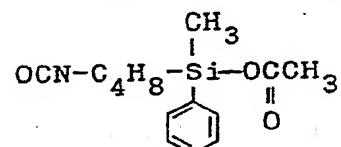
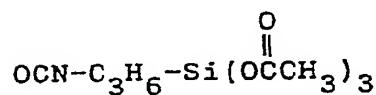
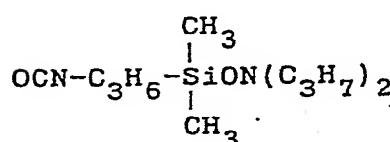
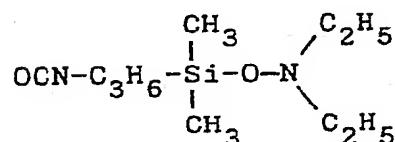
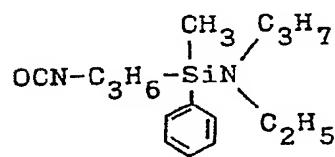
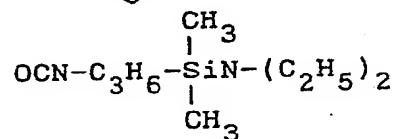
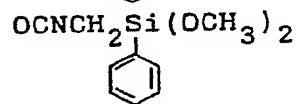
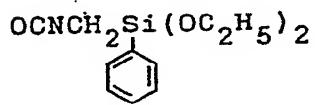
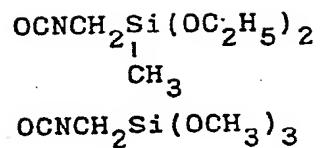


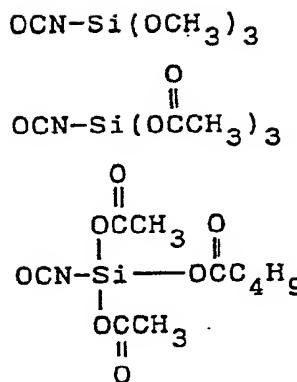
In the foregoing formula, R^8 and Y are as defined above and the groups Y are the same or different.

At least one of the groups Y is a hydrogen atom, a hydroxyl group or a hydrolyzable group, and b' is 0 or 1.

Examples of the compound of the formula (41) are those represented by the formulas

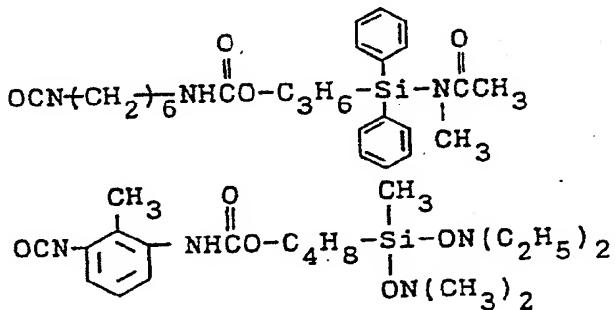






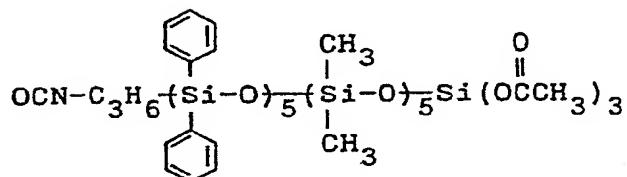
Also usable as the isocyanato-containing silane compound is a compound prepared by reacting the hydroxyl-containing silane compound with the polyisocyanate compound.

Examples of such isocyanato-containing silane compound include a reaction product of the compound of the formula (34) and a hexamethylene diisocyanate or tolylene diisocyanate, such as the compounds represented by the formulas



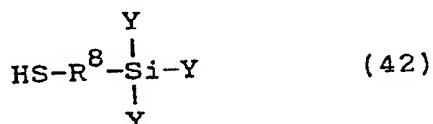
Useful isocyanato-containing silane compounds further include a condensation product of the isocyanato-

containing silane compound with, e.g. the polysilane compound, such as the compound represented by the formula



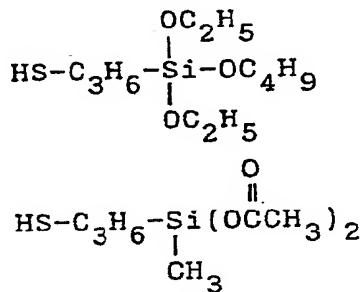
[Mercapto-containing silane compound]

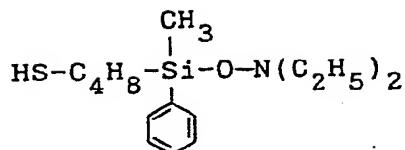
Examples of such compound include the compound represented by the formula (42)



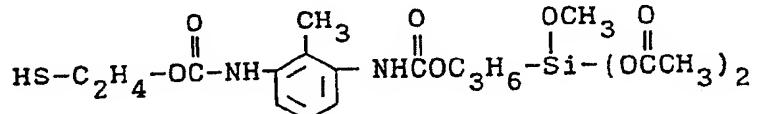
wherein R^8 and Y are as defined above, and the groups Y are the same or different, provided that at least one of the groups Y is a hydrogen atom, a hydroxyl group or a hydrolyzable group.

Specific examples of the compound of the formula (42) are those represented by the formula





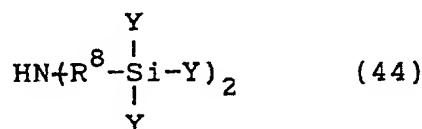
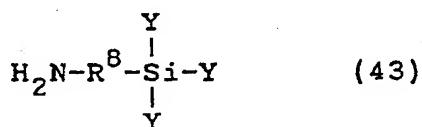
Also usable as the mercapto-containing silane compound is a reaction product prepared by reacting the hydroxyl-containing silane compound with the polyisocyanate compound and a thiochol compound (e.g. $\text{HS-C}_m\text{H}_{2m}-\text{OH}$ wherein m has the same meaning as above), such as the compound represented by the formula



Also usable is a condensation product of the mercapto silane compound with, e.g., a polysilane compound.

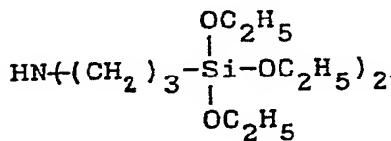
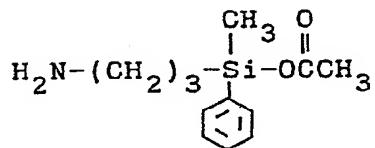
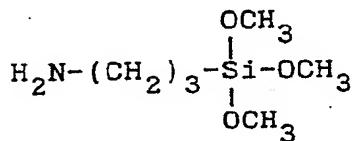
[NH or NH_2 group-containing silane compound]

Examples of such compound include the compounds represented by the formulas (43) and (44)

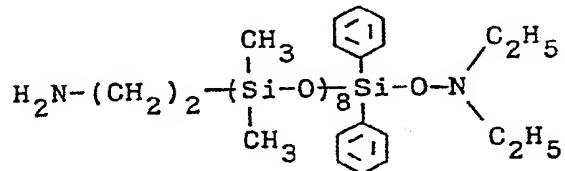


In the foregoing formulas, R^8 and Y are as defined above, the groups R^8 are the same or different, and the groups Y are the same or different, provided that at least one of the groups Y is a hydrogen atom, a hydroxyl group or a hydrolyzable group.

Specific examples of the compounds of the formulas (43) and (44) are those represented by the formulas



Also usable is a condensation product of the compound of the formula (43) or (44) with the polysilane compound, such as the compound represented by the formula

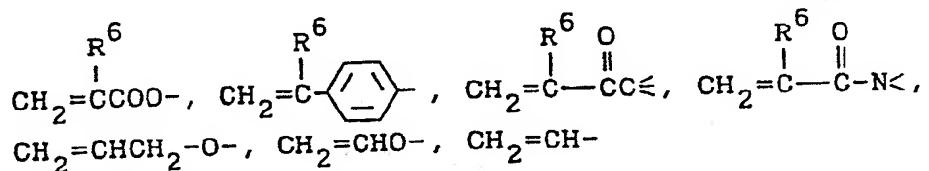


[Unsaturated group-containing silane compound]

Usable as such compound is a silane-containing polymerizable unsaturated monomer (g) to be described later.

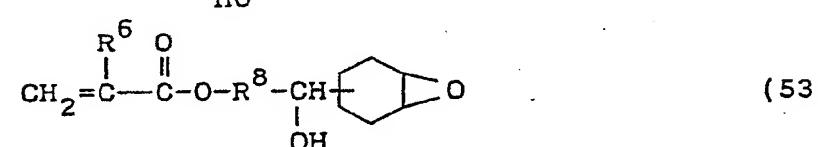
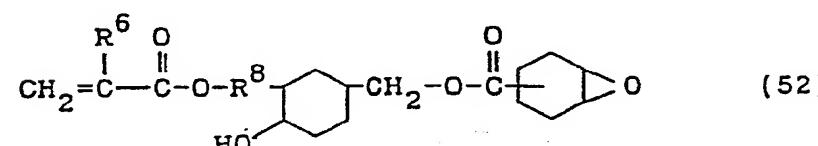
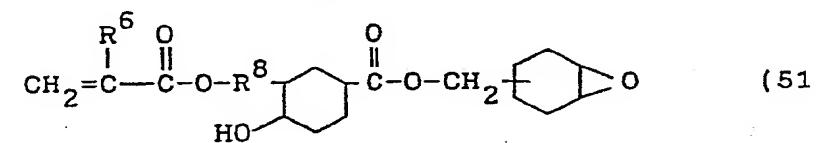
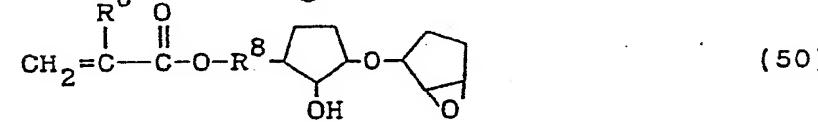
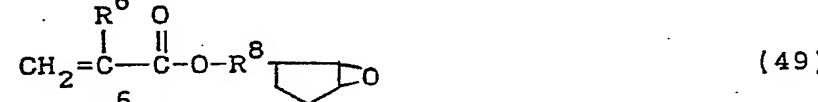
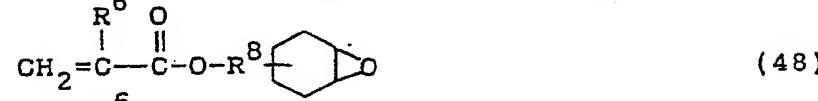
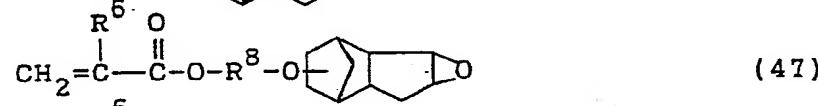
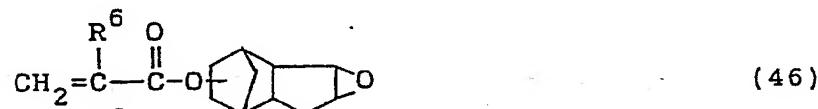
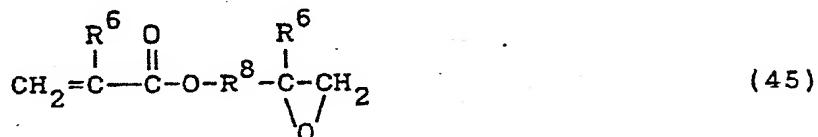
In addition to the resins prepared by reacting the resin (A) with the compounds (B) and (C), a copolymer is usable as the resin component (i) which copolymer is prepared by copolymerizing the hydroxyl-containing polymerizable unsaturated monomer (a), the epoxy-containing polymerizable unsaturated monomer (f), the silane-containing polymerizable unsaturated monomer (g) and when required the polymerizable unsaturated monomer (b) and the fluorine-containing polymerizable unsaturated monomer (c).

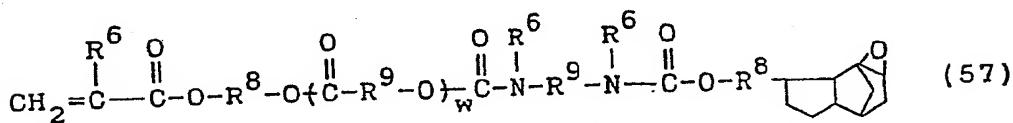
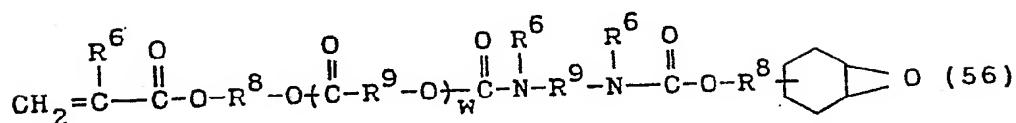
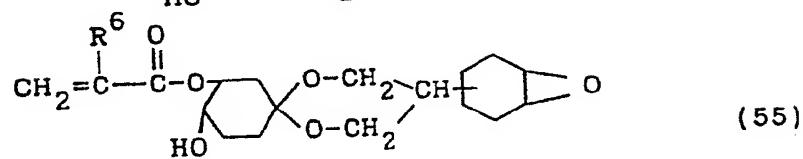
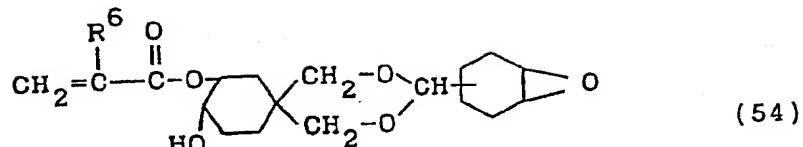
The epoxy-containing polymerizable unsaturated monomer (f) is a compound containing epoxy group and radically polymerizable unsaturated group in the molecule. The epoxy group may be alicyclic or aliphatic. Examples of the radically polymerizable unsaturated group include the groups represented by the formulas



In the foregoing formula, R^6 is as defined above.

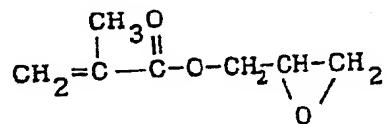
Examples of the epoxy-containing polymerizable unsaturated monomer having radically polymerizable unsaturated group $CH_2=C(R^6)COO-$ include the compounds represented by the formulas (45) to (57)

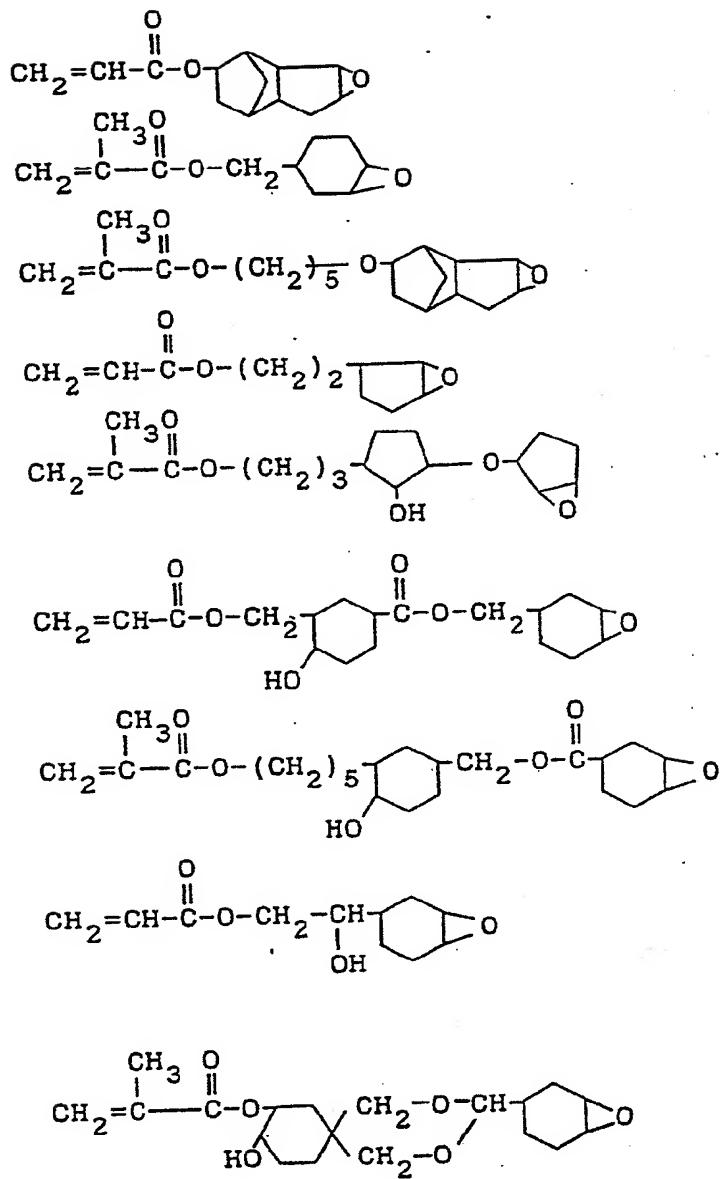




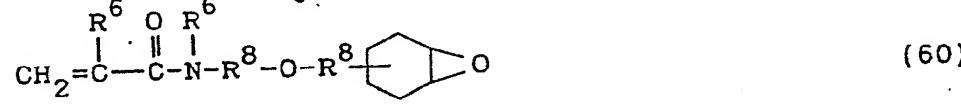
In the foregoing formula, R^6 , R^8 , R^9 and w are as defined above, the groups R^6 are the same or different, the groups R^8 are the same or different and the groups R^9 are the same or different.

Specific examples of the monomers of the formulas (45) to (57) are those represented by the formulas



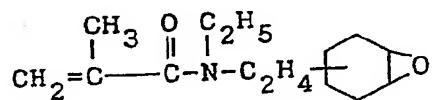
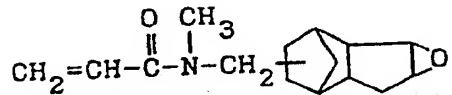


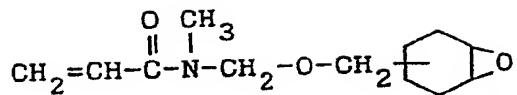
Examples of the epoxy-containing polymerizable unsaturated monomer having radically polymerizable unsaturated group $\text{CH}_2=\text{C}(\text{R}^6)-\text{C}(\text{O})-\text{N}^8$ are those represented by the formulas (58) to (60)



In the foregoing formulas, R^6 and R^8 are as defined above, the groups R^6 are the same or different, and the groups R^8 are the same or different.

Specific examples of the compounds of the formulas (58) to (60) include those represented by the formulas



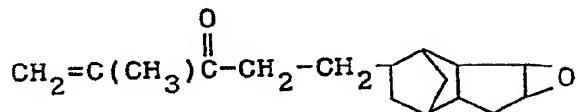


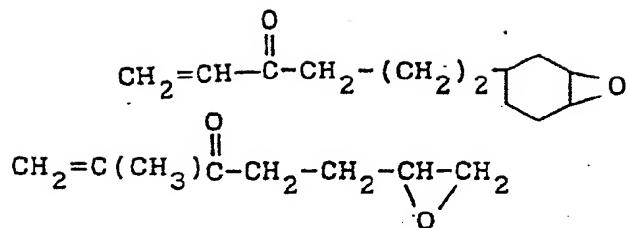
Examples of the epoxy-containing polymerizable unsaturated monomer having radically polymerizable unsaturated group $\text{CH}_2=\text{C}(\text{R}^6)-\text{C}(=\text{O})-\text{C}_2\text{H}_4\text{O}$ are inclusive of those represented by the formulas (61) to (63)



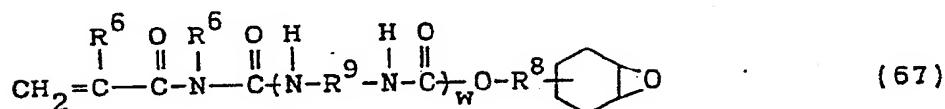
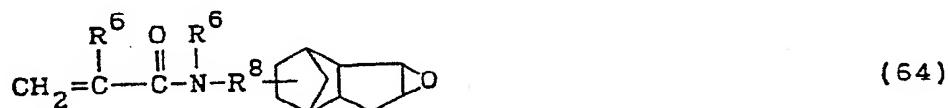
In the foregoing formulas, R^6 and R^8 are as defined above, the groups R^6 are the same or different, and the groups R^8 are the same or different.

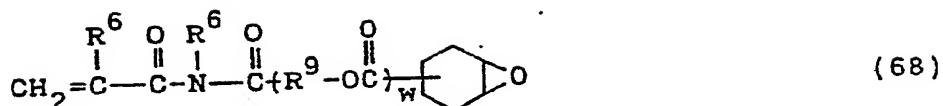
Specific examples of the compounds of the formulas (61) to (63) are those represented by the formulas





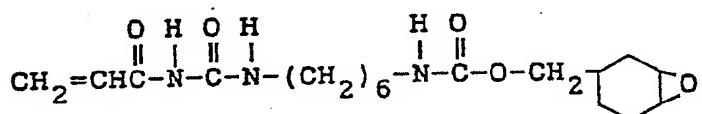
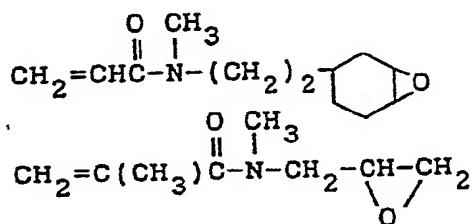
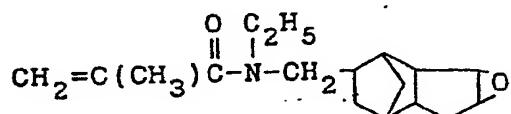
Examples of the epoxy-containing polymerizable unsaturated monomers having radically polymerizable unsaturated group $\text{CH}_2=\text{C}(\text{R}^6)-\overset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{N}-$ are those represented by the formulas (64) to (69)

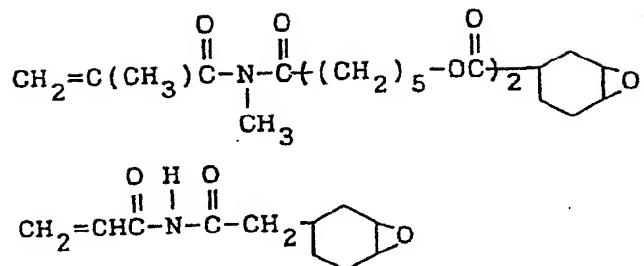




In the foregoing formula, R^6 , R^8 , R^9 and w are as defined above, the groups R^6 are the same or different, the groups R^8 are the same or different and the groups R^9 are the same or different.

Specific examples of the compounds of the formulas (64) to (69) are those represented by the formulas





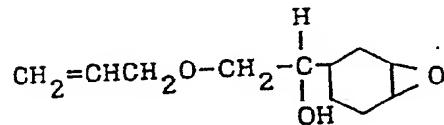
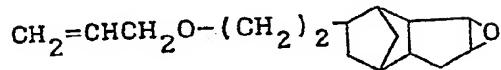
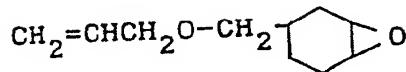
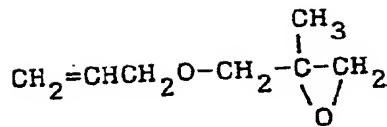
Examples of the epoxy-containing polymerizable unsaturated monomer having radically polymerizable unsaturated group $\text{CH}_2=\text{CHCH}_2\text{O}-$ are those represented by the formulas (70) to (73)



In the foregoing formulas, R^6 and R^8 are as defined above, and the groups R^8 are the same or different.

Specific examples of the compounds of the formulas (70) to (73) include those represented by the

formulas



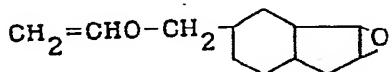
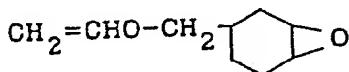
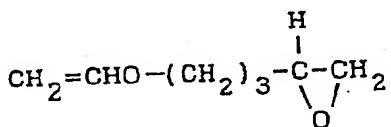
Examples of the epoxy-containing polymerizable unsaturated monomer having radically polymerizable unsaturated group $\text{CH}_2=\text{CHO}-$ are inclusive of those represented by the formulas (74) to (76)



In the foregoing formulas, R^6 and R^8 are as

defined above, and the groups R^8 are the same or different.

Specific examples of the compounds of the formulas (74) to (76) are those represented by the formulas

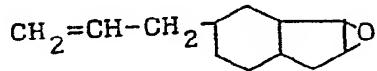
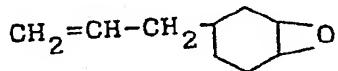
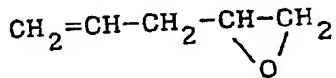


Examples of the epoxy-containing polymerizable unsaturated monomer having radically polymerizable unsaturated group $\text{CH}_2=\text{CH}-$ include the compounds represented by the formulas (77) to (79)

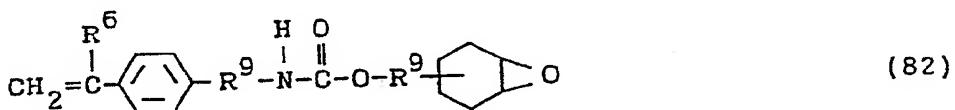
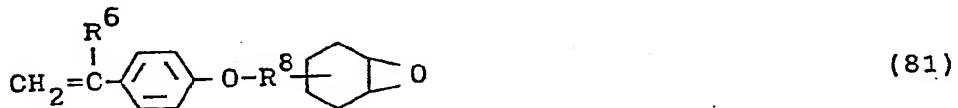


In the foregoing formulas, R^6 and R^8 are as defined above, and the groups R^8 are the same or different.

Specific examples of the compounds of the formulas (77) to (79) include those represented by the formulas



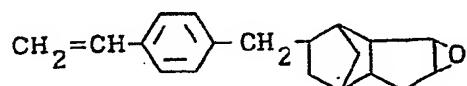
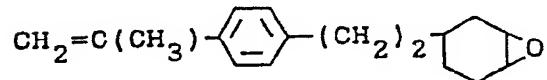
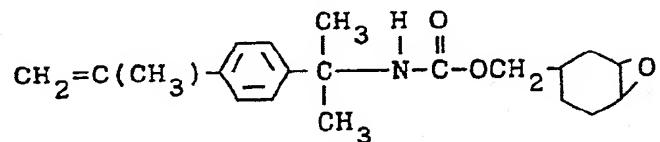
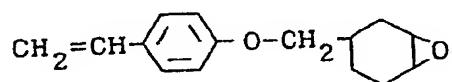
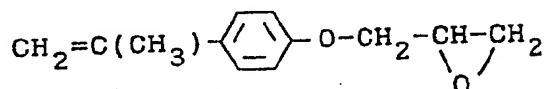
Examples of the epoxy-containing polymerizable unsaturated monomer having radically polymerizable unsaturated group $\text{CH}_2=\text{C}(R^6)-\text{C}_6\text{H}_4-$ include the compounds represented by the formulas (80) to (84)



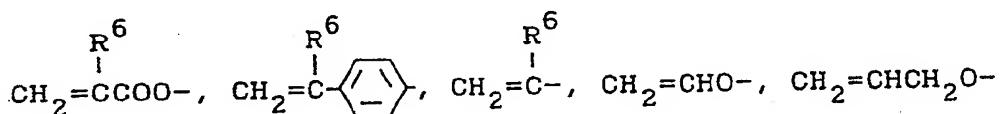


In the foregoing formulas, R^6 , R^8 and R^9 are as defined above, the groups R^6 are the same or different and the groups R^9 are the same or different.

Specific examples of the compounds of the formulas (80) to (84) include those represented by the formulas



The silane-containing polymerizable unsaturated monomer (g) is a compound having at least one silane group and radically polymerizable unsaturated group per molecule. Examples of the radically polymerizable unsaturated group are those represented by the formulas



wherein R^6 is as defined above.

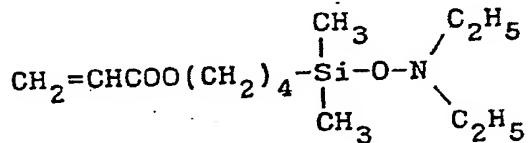
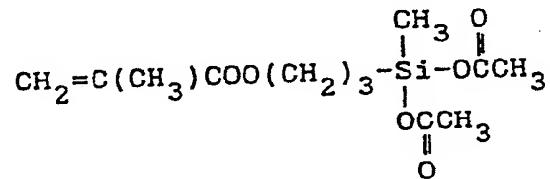
Examples of the silane-containing polymerizable unsaturated monomer having radically polymerizable unsaturated group $\text{CH}_2=\text{C}(\text{R}^6)-\text{COO}-$ include the compounds represented by the formula (85)



wherein R^6 , R^9 and Y are as defined above, the groups Y are the same or different and at least one of groups Y is a hydrogen atom, a hydroxyl group or a hydrolyzable group.

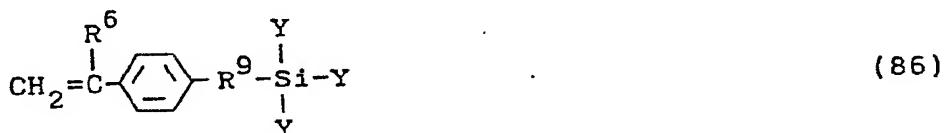
Examples of the compound of the formula (85) are γ -(meth)acryloxypropyltrimethoxysilane, γ -(meth)acryloxypropyltriethoxysilane,

γ -(meth)acryloxypropyltripropoxysilane,
 γ -(meth)acryloxypropylmethyldimethoxysilane,
 γ -(meth)acryloxypropylmethyldiethoxysilane,
 γ -(meth)acryloxypropylmethyldipropoxysilane,
 γ -(meth)acryloxybutylphenyldimethoxysilane,
 γ -(meth)acryloxybutylphenyldiethoxysilane,
 γ -(meth)acryloxybutylphenyldipropoxysilane,
 γ -(meth)acryloxypropyldimethylmethoxysilane,
 γ -(meth)acryloxypropyldimethylethoxysilane,
 γ -(meth)acryloxypropylphenylmethyldimethoxysilane,
 γ -(meth)acryloxypropylphenylmethylethoxysilane,
 γ -(meth)acryloxypropyltrisilanol,
 γ -(meth)acryloxypropylmethyldihydroxysilane,
 γ -(meth)acryloxybutylphenyldihydroxysilane,
 γ -(meth)acryloxypropyldimethylhydroxysilane,
 γ -(meth)acryloxypropylphenylmethylhydroxysilane, and the
compounds represented by the formulas



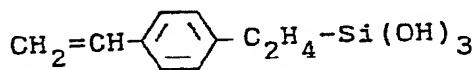
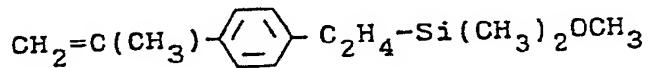
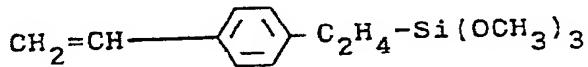
Examples of the silane-containing polymerizable

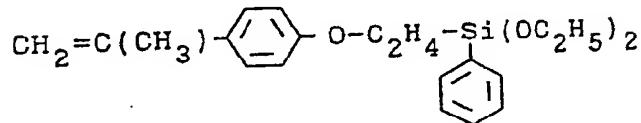
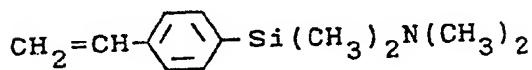
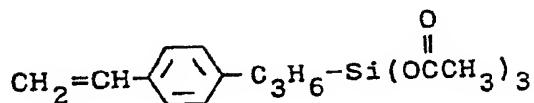
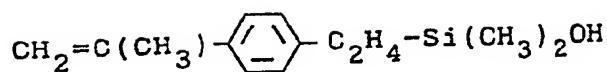
unsaturated monomer having radically polymerizable unsaturated group $\text{CH}_2=\text{C}(\text{R}^6)-\text{C}_6\text{H}_4-$ include the compounds represented by the formulas (86) to (88)



In the foregoing formulas, R^6 , R^9 and Y are as defined above, the groups Y are the same or different, and at least one of the groups Y is a hydrogen atom, a hydroxyl group or a hydrolyzable group.

Specific examples of the compounds of the formulas (86) to (88) include the compounds represented by the formulas





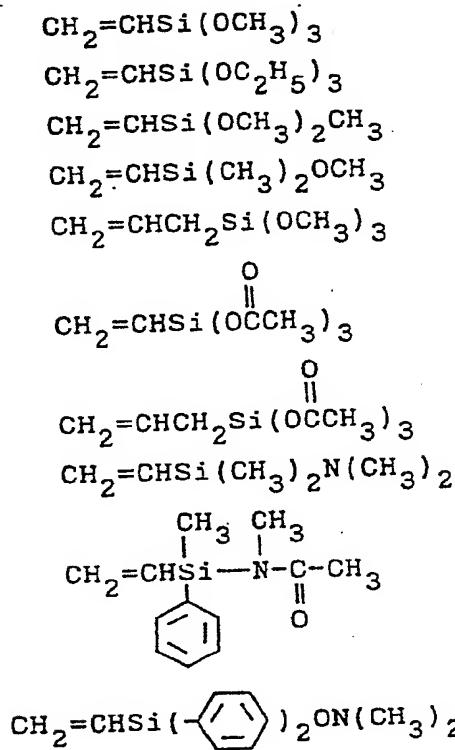
Examples of the silane-containing polymerizable unsaturated monomer containing radically polymerizable unsaturated group of the formula $\text{CH}_2=\text{C}(\text{R}^6)-$ include the compounds of the formulas (89) and (90)



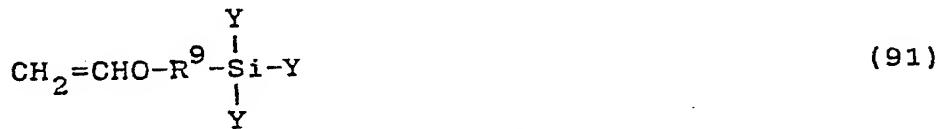
In the formulas (89) and (90), R^6 , R^9 and Y are as defined above, the groups Y may be the same or

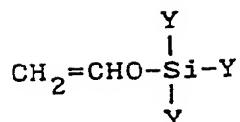
different and at least one of the groups Y is a hydrogen atom, a hydroxyl group or a hydrolyzable group.

Specific examples of the compounds of the formulas (89) and (90) are those represented by the formulas



Examples of the silane-containing polymerizable unsaturated monomer having radically polymerizable unsaturated group of the formula $\text{CH}_2=\text{CHO}-$ include the compounds represented by the formulas (91) and (92).

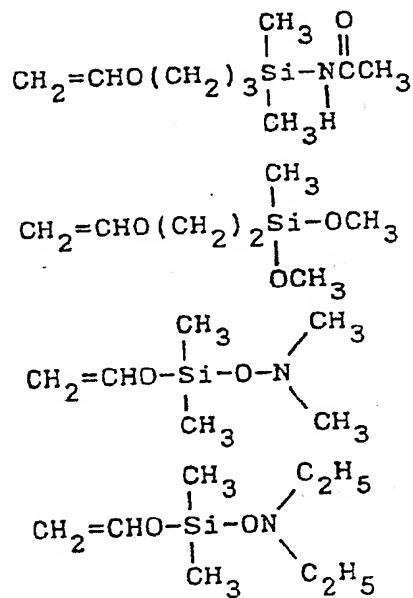




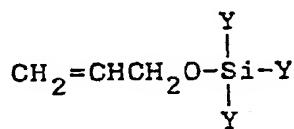
(92)

In the foregoing formulas, R^9 and Y are as defined above, the groups Y may be the same or different and at least one of the groups Y is a hydrogen atom, a hydroxyl group or a hydrolyzable group.

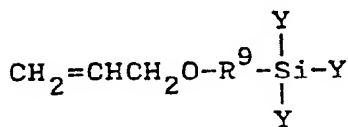
Specific examples of the compounds represented by the formulas (91) and (92) include those represented by the formulas



Examples of the silane-containing polymerizable unsaturated monomer having radically polymerizable unsaturated group of the formula $\text{CH}_2=\text{CHCH}_2\text{O}-$ include the compounds of the formulas (93) and (94)



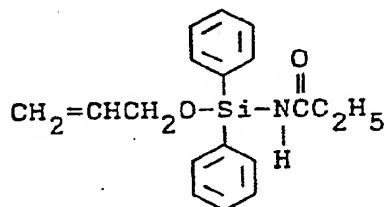
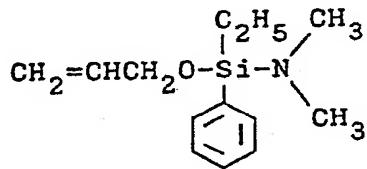
(93)

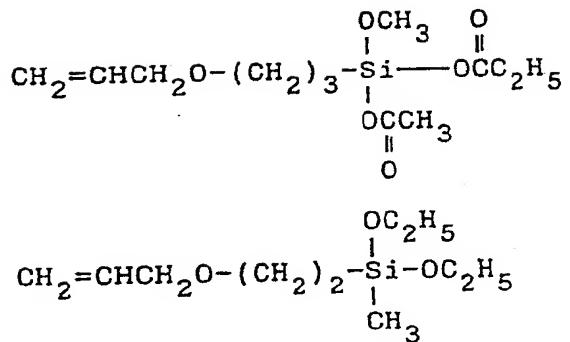


(94)

In the foregoing formulas (93) and (94), R^9 and Y are as defined above, the groups Y may be the same or different and at least one of the groups Y is a hydrogen atom, a hydroxyl group or a hydrolyzable group.

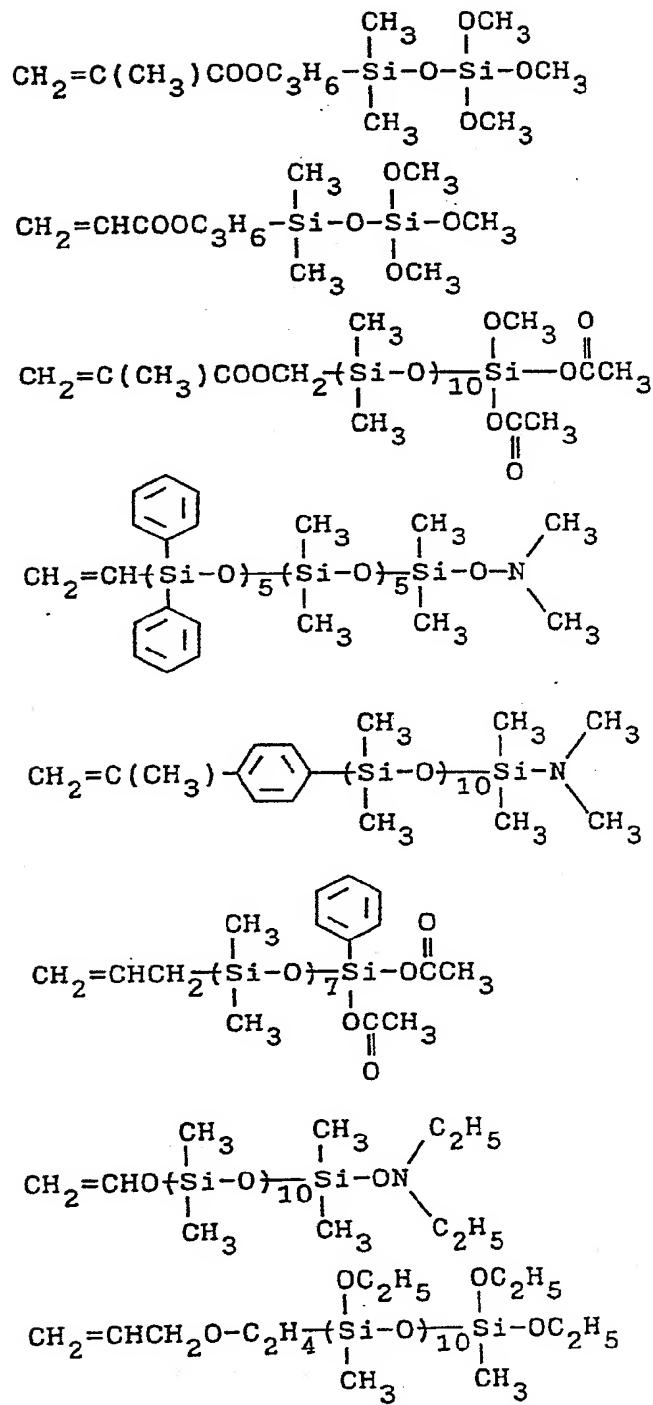
Specific examples of the compounds of the formulas (93) and (94) include those represented by the formulas

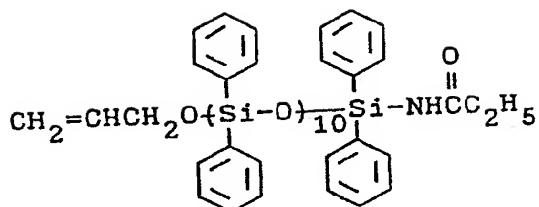




Also usable as the silane-containing polymerizable unsaturated monomer (g) is a polysiloxane unsaturated monomer containing silane group and polymerizable unsaturated group and prepared by reacting the silane-containing polymerizable unsaturated monomer with, for example, a polysilane compound such as the compounds of the formulas (38) to (40).

Representative of the polysiloxane unsaturated monomer is a polysiloxane macromonomer prepared by reacting about 30 to about 0.001 mole% of a compound of the formula (85) with about 70 to about 99.999 mole% of at least one of the compounds of the formulas (38) to (40) (for example those disclosed in GB 2202538A). Also useful as the polysiloxane unsaturated monomer are the compounds represented by the formulas





(ii) Resin component

The resin component (ii) is a mixture of a silane-containing resin or compound (hereinafter referred to as "resin (ii-1)") and an epoxy-containing resin or compound (hereinafter referred to as "resin (ii-2)"), at least one of resins (ii-1) and (ii-2) being a resin.

The resin (ii-1) has at least one silane group on the average in the molecule and the resin (ii-2) has at least one epoxy group on the average in the molecule. The resin or compound having less silane or epoxy group than said range reduces the curability of composition, hence undesirable.

The resins (ii-1) and (ii-2) of the resin component (ii) each have a number-average molecular weight of about 1,000 to about 200,000, preferably about 3,000 to about 80,000.

It is suitable to use as the resin (ii-1), for example, a silane-containing resin prepared from the starting materials useful for the resin component (i) such

that the resulting resin is free of epoxy.

Suitably usable as the resin (ii-2) is, for example, an epoxy-containing resin prepared from the starting materials for the resin component (i) such that the resulting resin is free of silane.

The proportions of the resins (ii-1) and (ii-2) are such that the resin component (ii) has an epoxy/silane ratio of between about 1/99 and about 99/1, preferably between about 1/5 and about 99/1. The resins (ii-1) and (ii-2) used in the ratio outside said range give a composition having a low curability and provide a coating film poor in resistance to xylol, hardness and mechanical properties, hence undesirable.

(iii) Resin component

The resin component (iii) contains at least one of each of hydroxyl, epoxy and silane groups on the average in the molecule and has a number-average molecular weight of about 1,000 to about 200,000, preferably about 3,000 to about 80,000. The number of hydroxyl group is preferably about 2 to about 400 on the average in the molecule in view of a high resistance to weather and water and the like. The epoxy and silane groups less than said range deteriorate the curability of composition, hence undesirable. The number-average molecular weight lower than about 1,000 impairs the physical properties, weather

resistance and the like, and the number-average molecular weight of more than about 200,000 increases the viscosity of composition, decreasing the amenability to coating operation, hence undesirable.

The resin component (i) containing hydroxyl group is usable as the resin component (iii). The hydroxyl groups in the resin component (i) can be any of those introduced into the resin component (i), those formed by reacting the resin (A) with the compound (B) or (C) (e.g., reacting epoxy and carboxyl groups), and those introduced by reacting the reaction product of the resin (A) and the compounds (B) and (C) (e.g. a product prepared by reacting an isocyanato-containing resin (A) with the hydroxyl-containing compounds (B) and (C) such that the resin contains an excess amount of isocyanato group) with a polyhydric alcohol.

(iv) Resin component

The resin component (iv) is a resin mixture of resins (ii-1) and (ii-2) useful for the resin component (ii) wherein one or both of them contain hydroxyl. Examples of combinations of resins or compounds constituting the resin component (iv) are a mixture of hydroxyl- and silane-containing resin/hydroxyl- and epoxy-containing resin, a mixture of hydroxyl- and silane-containing resin/epoxy-containing resin or compound, a

mixture of silane-containing resin or compound/hydroxyl- and epoxy-containing resin, etc.

The hydroxyl- and silane-containing resin contains at least one of each of hydroxyl and silane groups on the average in the molecule and has a number-average molecular weight of about 1,000 to about 200,000, preferably about 3,000 to about 80,000.

Less than one hydroxyl group on the average in the molecule decreases the curability of composition, hence undesirable. The number of hydroxyl group is preferably about 2 to about 400 on the average in the molecule in view of a high resistance to weather and water and the like. Less than one silane group impairs the curability of composition, hence undesirable. The molecular weight of less than 1,000 deteriorates the physical properties, weather resistance and the like, and the molecular weight of above 200,000 increases the viscosity of composition and impairs the amenability thereof to coating operation, hence undesirable.

The resin may be a silane- and hydroxyl-containing resin prepared from the starting materials useful for the resin component (iii) such that the resulting resin is free of epoxy.

The hydroxyl- and epoxy-containing resin contains at least one of each of hydroxyl and epoxy groups

on the average in the molecule and has a number-average molecular weight of about 1,000 to about 200,000, preferably about 3,000 to about 80,000.

Less than one hydroxyl group on the average in the molecule decreases the curability of composition, hence undesirable. The number of hydroxyl group is preferably about 2 to about 400 on the average in the molecule in view of a high resistance to weather and water and the like. Less than one epoxy group impairs the curability of composition, hence undesirable. The molecular weight of less than 1,000 deteriorates the physical properties, weather resistance and the like, and the molecular weight of above 200,000 increases the viscosity of composition and impairs the amenability thereof to coating operation, hence undesirable.

The resin may be an epoxy- and hydroxyl-containing resin prepared from the starting materials useful for the resin component (iii) such that the resulting resin is free of silane.

The proportions of the two resins or compounds in the resin component (iv) are such that the resin component (iv) has an epoxy/silane ratio of between about 1/99 and about 99/1, preferably between about 1/5 and about 99/1. The epoxy/silane ratio outside said range gives a composition with a low curability and forms a

coating film poor in resistance to xylol, hardness and mechanical properties, hence undesirable.

(v) Resin component

The resin component (v) can be any of the resin components (i) to (iv) which contains a hydroxyl-containing resin or compound.

The hydroxyl-containing resin or compound contains at least one hydroxyl group on the average in the molecule and has a number-average molecular weight of about 1,000 to about 200,000, preferably about 3,000 to about 80,000. Less than one hydroxyl group on the average in the molecule decreases the curability of composition, hence undesirable. The number of hydroxyl group is preferably about 2 to about 400 on the average in the molecule in view of a high resistance to weather and water and the like. The molecular weight of less than 1,000 deteriorates the physical properties and weather resistance, and the molecular weight of over 200,000 increases the viscosity of composition and impairs the amenability thereof to coating operation, hence undesirable.

Usable as the hydroxyl-containing resin is, for example, one useful as the resin component (i).

The hydroxyl-containing resin is used in such amount that at least one hydroxyl group is present per

silane or epoxy group.

The resin components described hereinbefore can be prepared by conventional methods. More specifically the reaction between hydroxyl and isocyanato groups, condensation reaction of silane group, copolymerization reaction and the like can be conducted in a conventional manner. For example, the reaction between isocyanato and hydroxyl groups is effected at a temperature between room temperature and 130°C for about 30 to about 360 minutes. The condensation reaction of silane group is conducted in the presence of an acid catalyst (for example, hydrochloric acid, sulfuric acid, formic acid, acetic acid or the like) with heating at a temperature of about 40 to about 150°C for about 1 to about 24 hours. The copolymerization reaction is carried out in the same manner under the same condicions as the reaction for synthesis of conventional acrylic or vinyl resins or the like. Such synthetic reaction can be performed, for example, by dissloving or dispersing the monomer component in an organic solvent and heating the solution or dispersion in the presence of a radical polymerization initiator at a temperature of about 60 to about 180°C with stirring. The reaction time usually ranges from about 1 to about 10 hours. Useful organic solvents include those inactive to the monomer or the compound to be used for

polymerization, such as ether solvents, ester solvents or hydrocarbon solvents. The hydrocarbon solvent is preferably used in combination with another solvent in view of a high solubility. The radical polymerization initiator can be any of polymerization initiators commonly employed and including peroxides such as benzoyl peroxide, t-butyl peroxy-2-ethylhexanoate and the like, and azo compounds such as 2,2'-azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile) and the like.

(I) resin component containing carboxyl group as well as the epoxy, sialne and hydroxyl groups are preferred because it results in increase of curability.

Also useful are modified resins prepared by chemically combining the resin component useful as (I) resin component with another resin (such as vinyl resin, polyester resin, urethane resin, silicone resin, epoxy resin or the like).

According to the invention, (I) resin component may be used as dissolved or dispersed in a solvent or in the form of a nonaqueous dispersion of polymer particles prepared in the presence of said resin component as a dispersion stabilizer. Examples of useful solvents are toluene, xylene and like hydrocarbon solvents; methyl ethyl ketone, methyl isobutyl ketone and like ketone solvents; ethyl acetate, butyl acetate and like ester

solvents; dioxane, ethylene glycol diethyl ether and like ether solvents; and butanol, propanol and like alcohol solvents.

The nonaqueous dispersion is described below in detail.

The nonaqueous dispersion can be prepared by polymerizing at least one radically polymerizable unsaturated monomer in the presence of a polymerization initiator and the dispersion stabilizer in an organic solvent in which the monomer and the dispersion stabilizer are soluble but the polymer particles formed by the polymerization are insoluble. The monomers as described hereinbefore are all usable for preparing the polymer present as the polymer particles in the non-aqueous dispersion. Since the polymer used as the particle component in the non-aqueous dispersion is not to be dissolved in the organic solvent used, it is desirable to use a copolymer prepared by polymerizing a predominant amount of monomer having a high polarity. Preferred monomers for use herein include methyl acrylate or methacrylate, ethyl acrylate or methacrylate, acrylonitrile, methacrylonitrile, 2-hydroxy acrylate, 2-hydroxy methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, acrylamide, methacrylamide, acrylic acid, methacrylic acid, itaconic acid, styrene, vinyl

toluene, α -methyl styrene, N-methylol acrylamide or methacrylamide and the like. The polymer particles contained in the non-aqueous dispersion can be crosslinked ones when desired. The polymer particles can be internally crosslinked by various methods, as by copolymerizing polyfunctional monomers such as divinylbenzene, ethylene glycol dimethacrylate or the like.

Organic solvents useful in preparation of the non-aqueous dispersion include those substantially incapable of dissolving the dispersed polymer particles prepared by the polymerization but capable of dissolving well the dispersion stabilizer and the radically polymerizable unsaturated monomers. Examples of useful organic solvents are pentane, hexane, heptane, octane, mineral spirit, naphtha and like aliphatic hydrocarbons; benzene, toluene, xylene and like aromatic hydrocarbons; alcohol solvents, ether solvents, ester solvents and ketone solvents such as isopropyl alcohol, n-butyl alcohol, isobutyl alcohol, octyl alcohol, cellosolve, butyl cellosolve, diethylene glycol monobutyl ether, methyl isobutyl ketone, diisobutyl ketone, ethyl acyl ketone, methyl hexyl ketone, ethyl butyl ketone, ethyl acetate, isobutyl acetate, acyl acetate, 2-ethylhexyl acetate, etc. These organic solvents can be used singly

or at least two of them are usable in mixture. Preferred solvents are combinations of a major amount of aliphatic hydrocarbon and a minor amount of aromatic hydrocarbon or the above-mentioned alcohol, ether, ester or ketone solvents. Trichlorotrifluoroethane, metaxylene-hexafluoride, tetrachlorohexafluorobutane and the like are also usable when so required.

The polymerization of the above monomers is conducted using a radical polymerization initiator. Useful radical polymerization initiators are, for example, 2,2'-azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile) and like azo-type initiators; and benzoyl peroxide, lauryl peroxide, tert-butyl peroctoate and like peroxide-type initiators. These polymerization initiators are used in an amount of about 0.2 to about 10 parts by weight per 100 parts by weight of the monomers to be polymerized. The amount of the dispersion stabilizer used for the polymerization is determinable over a wide range depending on the kind of the dispersion stabilizer. Generally it is suitable to use the radically polymerizable unsaturated monomer or monomers in an amount of about 3 to about 240 parts by weight, preferably about 5 to about 82 parts by weight, per 100 parts by weight of the dispersion stabilizer.

According to the present invention, the

dispersion stabilizer and the polymer particles are combined together, whereby the storage stability of the non-aqueous dispersion is improved and a coating film is formed which is outstanding in transparency, surface smoothness and mechanical properties. The dispersion stabilizer and the polymer particles can be combined together as by polymerizing the radically polymerizable unsaturated monomer(s) in the presence of the dispersion stabilizer having polymerizable double bond to cause concurrently the formation of polymer particles and the bonding of the resin to the polymer particles.

The polymerizable double bond can be most conveniently introduced into the dispersion stabilizer by adducting an acrylic acid, methacrylic acid, itaconic acid or like α, β -ethylenically unsaturated monocarboxylic acid to some of epoxy groups present in the dispersion stabilizer. Also the introduction can be effected by adducting isocyanoethyl methacrylate or like isocyanato-containing monomer to the hydroxyl group contained in the dispersion stabilizer.

The dispersion stabilizer can be combined with the polymer particles also using a reactive monomer as a monomer component for formation of polymer particles, such as γ -methacryloxypropyl trimethoxysilane, γ -methacryloxypropyl triethoxysilane, γ -acryloxypropyl trimethoxy-

silane, γ -methacryloxybutyl triethoxysilane, γ -acryloxypropyl trisilanol or the like.

When the dispersion stabilizer is a 2- or 3-component resin or compound, the nonaqueous dispersion is prepared by polymerizing the radically polymerizable unsaturated monomer or monomers in the presence of such mixture as a dispersion stabilizer. Optionally the nonaqueous dispersion can be prepared by polymerizing the radically polymerizable unsaturated monomer or monomers in the presence of a portion of 2- or 3-component (1- or 2-component) resin or compound as a dispersion stabilizer, and admixing the rest of the resin or compound with the polymer thus formed.

Described below is (II) crosslinking agent which is at least one substance selected from carboxylic compounds, polyisocyanate compounds and aminoaldehyde resins and which combines with (I) resin component and (III) curing catalyst to provide the curable composition of the invention.

The crosslinking agent is mixed with (I) resin component dissolved or dispersed in the solvent or present as the dispersion stabilizer in the nonaqueous dispersion of polymer particles. (II) crosslinking agent can be incorporated into the nonaqueous dispersion also by mixing with (I) resin component as the dispersion stabilizer

before preparation of nonaqueous dispersion.

Carboxylic acid compounds for use as the crosslinking agent in the invention include, for example, a resin or compound having at least 2 carboxyl groups on the average in the molecule, or a resin or compound having at least one carboxylic anhydride group on the average in the molecule. The carboxylic acid compound has a number-average molecular weight of about 100 to about 200,000, preferably about 100 to about 100,000.

Carboxylic acid compounds useful in the invention include those given below in (1) to (8).

(1) Carboxylic acid

Examples of useful carboxylic acids are phthalic acid, isophthalic acid, terephthalic acid, tetrahydronaphthalic acid, tetrahydrotetraphthalic acid, hexahydroisophthalic acid, hexahydroterephthalic acid, trimellitic acid, hexahydrotetramellitic acid, pyromellitic acid, cyclohexanetetracarboxylic acid, methyl tetrahydronaphthalic acid, methyl cyclohydronaphthalic acid, endomethylenehexahydronaphthalic acid, methylendomethylene-tetrahydronaphthalic acid, maleic acid, fumaric acid, itaconic acid, succinic acid, glutaric acid, adipic acid, azelaic acid, sebamic acid, decanedicarboxylic acid, suberic acid, pimelic acid, dimer acid (dimer of tall oil fatty acid), tetrachlorophthalic acid,

naphthalenedicarboxylic acid, 4,4'-diphenylmethane-dicarboxylic acid, 4,4'-dicarboxybiphenyl and the like, and the corresponding anhydrides.

(2) Polyester resin

Useful polyester resins include, for example, resins prepared from a mixture of a carboxylic acid selected from the examples given above in (1) and a polyhydric alcohol to be exemplified below.

Examples of useful polyhydric alcohols are ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, 1,4-butanediol, 1,3-butanediol, 2,3-butanediol, 1,2-butanediol, 1,5-pantanediol, 1,4-pantanediol, 2,4-pantanediol, 2,3-dimethyltrimethylene glycol, tetramethylene glycol, 3-methyl-4,5-pantanediol, 2,2,4-trimethyl-1,3-pantanediol, 1,6-hexanediol, 1,5-hexanediol, 1,4-hexanediol, 2,5-hexanediol, 1,4-cyclohexanediethanol, neopentyl glycol, hydroxypivalate neopentyl glycol, polyalkylene oxide, bishydroxyethyl terephthalate, adduct of (hydrogenated) bisphenol A with alkylene oxide, glycerin, trimethylolpropane, trimethylolethane, diglycerin, pentaerythritol, dipentaerythritol, sorbitol, etc.

It is possible to use, conjointly with the above carboxylic acid compounds and polyhydric alcohols, Cardura E 10 (trademark for product of Shell Chemical Co., Ltd.),

α -olefinepoxide, butyleneoxide, Epon #828 (trademark for product of Shell Chemical Co., Ltd.), Epon #1001 (trademark for product of Shell Chemical Co., Ltd.) and like epoxy-containing compounds, dimethylol propionic acid, pivalic acid, 12-hydroxystearic acid, ricinolic acid and like compounds having hydroxyl and carboxyl groups in the molecule; ϵ -caprolactone, δ -methyl- δ -valerolactone, γ -valerolactone, δ -valerolactone, δ -caprolactone, γ -butyrolactone and like lactones; benzoic acid, p-t-butylbenzoic acid, abietic acid, acetic acid, propionic acid, butyric acid, caproic acid and like monocarboxylic acids; 2-ethylhexanol, lauryl alcohol, stearyl alcohol and like monohydric higher alcohols; coconut oil, cottonseed oil, rice bran oil, fish oil, tall oil, soybean oil, linseed oil, tung oil, rapeseed oil, castor oil, dehydrated castor oil, fatty acids thereof, dimers thereof, trimers thereof (these being optionally hydrogenated ones), etc.

(3) Carboxyl-containing vinyl resin

The carboxyl-containing vinyl resins described hereinbefore as useful for the resin component (i) can be used as such resin.

(4) Carboxyl- and fluorine-containing resin

The carboxyl- and fluorine-containing resins described hereinbefore as useful for the resin component

(i) can be used as such resins.

(5) Carboxyl-containing urethane resin

Useful resins include a reaction product of a resin or compound containing hydroxyl and carboxyl groups in the molecule (such as the hydroxyl- and carboxyl-containing compounds mentioned above in (2) polyester resin and the polyester resin, carboxyl-containing vinyl resin and the carboxyl- and fluorine-containing resin, all described above in (2), (3) and (4), respectively and each prepared such that the resulting resin contains hydroxyl group) with, e.g. the polyisocyanate compound (such as polyisocyanate compounds exemplified hereinbefore as useful for the isocyanato-containing resin to be used for the resin component (i)).

(6) Carboxyl-containing silicone resin

Useful resins include resins prepared by modifying one of the polyester resin, carboxyl-containing resin and carboxyl- and fluorine-containing resin all mentioned above in (2), (3) and (4) respectively and each prepared such that the resulting resin contains hydroxyl group, with a silicone resin or a hydrolyzable silyl-containing compound such as methyltrimethoxysilane, methyltriacetoxy silane, dimethyldimethoxysilane or the like, examples of the silicone resin being those available under Z-6018 and Z-6118 (trademarks for products of Dow

Corning Ltd.), and SH-5050, SH-6018 and SH-6188 (trademarks for products of Toray Silicone Co., Ltd.).

(7) Carboxyl-containing polyether resin

Useful resins include an adduct of the acid anhydride exemplified above with a polyoxyalkylene polyol such as polyethylene glycol, polypropylene glycol, polytetramethylene glycol or the like.

(8) Carboxyl-containing epoxy resin

Useful resins include an adduct of the polycarboxylic acids exemplified above as the polycarboxylic acid compound mentioned above in (1) with an epoxy compound such as Epon #828 (trademark for epoxy resin of Shell Chemical Co., Ltd.), Epon #1001 (trademark for epoxy resin of Shell Chemical Co., Ltd.), diglycidyl ether or the like.

The amount of the carboxylic acid compound used in the invention is about 1 to about 40 parts by weight, preferably about 3 to about 30 parts by weight, more preferably about 5 to about 25 parts by weight, per 100 parts by weight of (I) resin component. Use of more than 40 parts by weight of the acid decreases the storage stability of the curable composition, and use of less than 1 part by weight of the acid impairs the adhesion to metals and coating films, hence undesirable.

Polyisocyanate compounds useful as the

crosslinking agent in the invention include those which have in the molecule at least 2, preferably 2 or 3 isocyanato groups and which can be any of aliphatic, alicyclic, aromatic and aromatic-aliphatic compounds. Examples of useful polyisocyanate compounds are hexamethylene diisocyanate, trimethylhexamethylene diisocyanate and like aliphatic diisocyanates; (hydrogenated) xylylene diisocyanate, isophorone diisocyanate and like alicyclic diisocyanates; and tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate and like aromatic diisocyanates. Also usable are an adduct of the diisocyanate compound with a polyhydric alcohol, low-molecular weight polyester resin or water; a polymer of diisocyanate compounds with each other; isocyanate biurets of such diisocyanate compounds, etc. Representative commercial products of these compounds are those available under the trademarks: "BURNOCK D-750, -800, DN-950 and DN-970" (products of Dainippon Ink And Chemicals Incorporated), "SUMIDUL L, N, HL, IL and N-3390" (products of Sumitomo Bayer AG), "TAKENATE D-102, -202, -110N and -123N" (products of Takeda Chemical Industries, Ltd.), "COLONATE-L, -HL, -EL and -203" (products of Nippon Polyurethane Kogyo K.K.), "DECORANATE 24A-90CX" (product of Asahi Chemical Industry Co., Ltd.), etc.

Examples of the polyisocyanate compound include

blocked polyisocyanate compounds prepared by blocking the polyisocyanate compound with a blocking agent such as aliphatic or aromatic monohydric alcohol oxime, lactam, phenol or the like. Specific examples of such compounds are TAKENATE B-815N (trademark for product of Takeda Chemical Industries, Ltd.), BURNOCK D-550 (trademark for product of Dainippon Ink And Chemicals Incorporated), ADITOL VXL-80 (trademark for product of Hoechst AG, West Germany), COLONATE-2507 (trademark for product of Nippon Polyurethane Kogyo K.K.), etc.

A suitable amount of the polyisocyanate compound used is about 1 to about 30 parts by weight, preferably about 2 to about 20 parts by weight, per 100 parts by weight of (I) resin component (calculated as solids). The amount smaller than said range fails to improve the mechanical properties of the coating film and the adhesion to plastic substrates (such as urethane ones), hence undesirable.

When required, a curing catalyst for the polyisocyanate compound can be used. Examples of useful curing catalysts are dibutyltin diacetate, dibutyltin dioctate, dibutyltin dilaurate and like organotin compounds, and triethylamine, diethanolamine and like amine compounds, etc. The amount of the curing catalyst used is preferably about 0.01 to about 10 parts by weight

per 100 parts by weight of (I) resin component (calculated as solids).

Examples of aminoaldehyde resins useful as the crosslinking agent in the invention are a condensation product prepared by condensing an amino compound with an aldehyde compound by conventional methods; and an aminoaldehyde resin prepared by modifying the condensate with an alcohol. Examples of the amino compound are melamine, urea, benzoguanamine, spiroguanamine, acetoguanamine, steroguanamine, etc. Examples of the aldehyde compound are formaldehyde, paraformaldehyde, acetoaldehyde, etc. While C_{1-4} monohydric alcohol is desirable as the alcohol for the modification in view of low-temperature curability, usable in combination therewith are 2-ethylhexanol, cyclohexanol, lauryl alcohol, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monoethyl ether and like alcohols containing at least 5 carbon atoms.

Melamine resins are most suitable among the above aminoaldehyde resins when a coating film of high weatherability is required. Examples of useful melamine resins are hexamethyl etherified methylol melamine, hexabutyl etherified methylol melamine, hexamethylbutyl etherified methylol melamine, methyl etherified methylol melamine, n-butyl etherified methylol melamine, i-

butylated methyol melamine, etc. Commercially available products of such melamines are Cymel-303, Cymel-235, Cymel-238, Cymel-1130, Cymel-254 and Cymel-327 (trademarks for melamine resins manufactured by Mitsui Cyanamide Co., Ltd.), Sumimal M-55, Sumimal M-100 and Sumimal M-40S (trademarks for melamine resins of Sumitomo Chemicals Co., Ltd.), U-Van 20SE-60, U-Van 225 and U-Van 28SE-60 (trademarks for melamine resins manufactured by Mitsui Toastu Chemicals Inc.), Superbeckamin G-840, Superbeckamin G-821-60 and Superbeckamin L-127-75 (trademarks for melamine resins manufactured by Dainippon Ink And Chemicals Inc.).

A suitable amount of the aminoaldehyde resin used is about 1 to about 50 parts by weight, preferably about 3 to about 40 parts by weight, more preferably about 5 to about 30 parts by weight, per 100 parts by weight of (I) resin component (calculated as solids). The amount above said range reduces the curability of composition, whereas the amount below the range tends to deteriorate the coating suitability in conjoint application with an aminoalkyd (polyester) coating composition or an aminoacryl coating composition, hence undesirable.

The term "coating suitability" used herein is intended to denote the adhesion between the topcoat of the curable composition of the invention and the undercoat of

the aminoalkyd or aminoacryl coating composition, and the appearance properties of a coating film formed on applying these compositions by a wet-on-wet coating method.

It remains to be clarified why the curable composition of the invention exhibits an excellent coating suitability with conventionally employed aminoalkyd (polyester) coating compositions, aminoacryl coating compositions and like compositions. Presumably this feature may be attributable to the amenability of the composition of the invention to similar substances (aminoaldehyde resin).

Further the use of aminoaldehyde resin results in coating of high curability due to the reaction between the aminoaldehyde resin and the hydroxyl group present in the curable composition and also to the self-condensation reaction of aminoaldehyde resin. These reactions can be accelerated by use of a catalyst which can be any of conventional ones such as carboxylic acid compounds, phosphoric acid compounds, sulfonic acid compounds, salts of these compounds with basic compounds, etc.

Described below is (III) curing catalyst which is used conjointly with (I) resin component and (II) crosslinking agent to provide the curable composition of the invention. (III) curing catalyst is at least one compound selected from the group consisting of

organometallic compounds, Lewis acids, protonic acids and compounds with Si-O-Al bonds.

The curing catalyst is admixed with the other essential ingredients for the curable composition of the invention in a suitable manner without specific limitation.

(1) Organometallic compound

Useful organometallic compounds include metal alkoxide compounds, metal chelate compounds, metal alkyl compounds, etc.

[Metal alkoxide compound]

Useful metal alkoxide compounds include the compounds having alkoxy group attached to a metal such as aluminum, titanium, zirconium, calcium, barium or the like. These compounds may contain an association of molecules. Preferred metal alkoxide compounds include, for example, aluminum alkoxide, titanium alkoxide and zirconium alkoxide. Specific examples of such compounds are exemplified below.

Useful aluminum alkoxide compounds include those represented by the formula



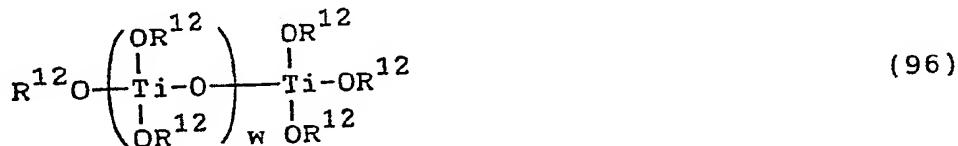
wherein the groups R^{12} are the same or different and each

represent an alkyl group having 1 to 20 carbon atoms or an alkenyl group.

Examples of the alkyl group having 1 to 20 carbon atoms include nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, octadecyl and the like as well as the examples of alkyl groups of 1 to 8 carbon atoms given hereinbefore. Examples of the alkenyl group are vinyl, allyl and the like.

Examples of the aluminum alkoxide having the formula (95) are aluminum trimethoxide, aluminum triethoxide, aluminum tri-n-propoxide, aluminum triisopropoxide, aluminum tri-n-butoxide, aluminum triisobutoxide, aluminum tri-sec-butoxide, aluminum tri-tert-butoxide and the like. Among them, preferable are aluminum triisopropoxide, aluminum tri-sec-butoxide, aluminum tri-n-butoxide, etc.

Useful titanium alkoxide compounds include the titanates represented by the formula



wherein w and R¹² are as defined above.

Examples of the titanate of the formula (96) wherein w is 0 are tetramethyl titanate, tetraethyl

titanate, tetra-n-propyl titanate, tetraisopropyl titanate, tetra-n-butyl titanate, tetraisobutyl titanate, tetra-tert-butyl titanate, tetra-n-pentyl titanate, tetra-n-hexyl titanate, tetraisoctyl titanate, tetra-n-lauryl titanate, etc. Suitable results can be achieved by use of tetraisopropyl titanate, tetra-n-butyl titanate, tetra-isobutyl titanate, tetra-tert-butyl titanate or the like. Of the titanates wherein w is 1 or more, those which can achieve good results are dimers to hendecamers (w = 1 to 10 in the formula (96)) of tetraisopropyl titanate, tetra-n-butyl titanate, tetraisobutyl titanate, tetra-tert-butyl titanate or the like.

Useful zirconium alkoxide compounds include those represented by the formula



wherein w and R¹² are as defined above.

Examples of the zirconate of the formula (97) wherein w is 0 are tetraethyl zirconate, tetra-n-propyl zirconate, tetraisopropyl zirconate, tetra-n-butyl zirconate, tetra-sec-butyl zirconate, tetra-tert-butyl zirconate, tetra-n-pentyl zirconate, tetra-tert-pentyl zirconate, tetra-tert-hexyl zirconate, tetra-n-heptyl

zirconate, tetra-n-octyl zirconate, tetra-n-stearyl zirconate and the like. Suitable results can be obtained by use of tetraisopropyl zirconate, tetra-n-propyl zirconate, tetraisobutyl zirconate, tetra-n-butyl zirconate, tetra-sec-butyl zirconate, tetra-tert-butyl zirconate or the like. Of the zirconates wherein w is 1 or more, those which can produce suitable results are dimers to hendecamers (w = 1 to 10 in the formula (97)) of tetraisopropyl zirconate, tetra-n-propyl zirconate, tetra-n-butyl zirconate, tetraisobutyl zirconate, tetra-sec-butyl zirconate, tetra-tert-butyl zirconate or the like. The zirconium alkoxide compound may contain an association of such zirconates as a constituent unit.

[Metal chelate compound]

Preferred metal chelate compounds include, for example, aluminum chelate compounds, titanium chelate compounds and zirconium chelate compounds. Among these chelate compounds, preferred are those containing as a ligand for forming a stable chelate ring a compound capable of forming a keto-enol tautomer.

Examples of the compound capable of forming a keto-enol tautomer are β -diketones (such as acetyl acetone), esters of acetoacetic acids (such as methyl acetoacetate), esters of malonic acids (such as ethyl malonate), ketones having hydroxyl group in the β -position

(such as diacetone alcohol), aldehydes having hydroxyl group in the β -position (such as salicylaldehyde), esters having hydroxyl group in the β -position (such as methyl salicylate), etc. The use of esters of acetoacetic acids or β -diketones can achieve suitable results.

The aluminum chelate compound can be suitably prepared for example by admixing about 3 moles or less of the compound capable of forming a keto-enol tautomer with about 1 mole of the aluminum alkoxide, followed when required by heating. Examples of preferred aluminum chelate compounds for use in the invention are tris(ethylacetoacetate)aluminum, tris(n-propylacetoacetate)aluminum, tris(isopropylacetoacetate)aluminum, tris(n-butylacetoacetate)aluminum, isopropoxy-bis(ethylacetoacetate)aluminum, diisopropoxyethylacetoacetate aluminum, tris(acetylacetonato)aluminum, tris(propionylacetonato)aluminum, diisopropoxypropionyl-acetonato aluminum, acetylacetonato-bis(propionyl-acetonato)aluminum, monoethylacetoacetate-bis(acetyl-acetonato)aluminum, tris(acetylacetonato)aluminum and the like.

The titanium chelate compound can be suitably prepared for example by admixing about 4 moles or less of the compound capable of forming a keto-enol tautomer with about 1 mole of the titanium alkoxide, followed when

required by heating. Examples of preferred titanium chelate compounds are diisopropoxy-bis(ethylacetacetate)-titanate, diisopropoxy-bis(acetylacetato)titanate, diisopropoxy-bis(acetylacetato)titanate, etc.

The zirconium chelate compound can be suitably prepared for example by admixing about 4 moles or less of the compound capable of forming a keto-enol tautomer with about 1 mole of the zirconium alkoxide, followed when required by heating. Examples of preferred zirconium chelate compounds for use in the invention are tetrakis(acetylacetato)zirconium, tetrakis (n-propylacetacetate)zirconium, tetrakis(acetylacetato)-zirconium, tetrakis(ethylacetacetate)zirconium and the like.

The aluminum chelate compounds, zirconium chelate compounds and titanium chelate compounds can be used singly or at least two of them are usable in mixture.

[Metal alkyl compound]

The compound has alkyl group, preferably C₁-20 alkyl group, bonded to a metal such as aluminum, zinc or the like. Examples of such compound are triethyl aluminum, diethyl zinc, etc.

(2) Lewis acid

Useful Lewis acids include metal halides, compounds having metal, halogen and other substituents,

and complexes of these compounds. Specific examples of such compounds are:

AlCl_3 , AlF_3 , AlEtCl_2 , AlEt_2Cl , TiCl_4 , TiBr_4 ,
 TiF_4 , ZrCl_4 , ZrBr_4 , ZrF_4 , SnCl_4 , FeCl_3 , SbCl_3 , SbCl_5 ,
 PCl_3 , PCl_5 , GaCl_3 , GaF_3 , InF_3 , BCl_3 , BBr_3 , BF_3 ,
 $\text{BF}_3:(\text{OC}_2\text{H}_5)_2$, $\text{BF}_4:(\text{OC}_2\text{H}_5)_3$, $\text{BCl}_3:(\text{OC}_2\text{H}_5)_2$, $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_5$,
 $\text{BF}_3:\text{NH}_2\text{C}_2\text{H}_4\text{OH}$, $\text{BF}_3:\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, $\text{PF}_6\text{S}(\text{C}_6\text{H}_5)_3$

(3) Protonic acid

Useful protonic acids include organic protonic acids such as methanesulfonic acid, ethanesulfonic acid, trifluoromethanesulfonic acid, benzenesulfonic acid, p-toluenesulfonic acid and the like, and inorganic protonic acids such as phosphoric acid, phosphorus acid, phosphinic acid, phosphonic acid, sulfuric acid, perchloric acid and the like.

(4) Compound having Si-O-Al bond or bonds

Specific examples of such compounds include aluminum silicate.

Among the curing catalysts described above, a metal chelate compound is preferred because it can form a coating composition having a high curability.

A suitable amount of each curing catalyst used among those described above in (1) to (3) is about 0.01 to about 30 parts by weight per 100 parts by weight of

combined amount of (I) resin component and (II) crosslinking agent, calculated as solids. Less than about 0.01 part by weight of the catalyst is likely to decrease the curability and over about 30 parts thereof tends to remain in the cured product and to reduce the water resistance, hence undesirable. A preferred amount of the catalyst is about 0.1 to about 10 parts by weight and a more preferred one is about 1 to about 5 parts by weight.

A suitable amount of the curing catalyst stated above in (4) is about 1 to about 100 parts by weight per 100 parts by weight of combined amount of (I) resin component and (II) crosslinking agent, calculated as solids. The amount less than the range tends to reduce the curability and the amount above the range tends to impair the properties of the coating film, hence undesirable.

When required, the curable composition of the invention may contain a chelating agent, polyepoxy compound, polysilane compound, organic solvent, pigment, additive resin and the like. The chelating agent is used to improve the storage stability and can be any of the above-exemplified chelate compounds. The polyepoxy compound and polysilane compound are used to enhance the curability of coating composition and can be any of those described hereinbefore.

Preferred organic solvents include those having a boiling point of 150°C or less in view of a high curing rate of the curable composition, but are not specifically limited to the above. Preferable organic solvents are toluene, xylene and like hydrocarbon solvents; methyl ethyl ketone, methyl isobutyl ketone and like ketone solvents; ethyl acetate, butyl acetate and like ester solvents; dioxane, ethylene glycol diethyl ether and like ether solvents; and butanol, propanol and like alcohol solvents. While these solvents may be used alone or in a suitable combination, alcohol solvents are preferably used in mixture with another solvent in view of a high solubility of the resin. The resin concentration in the solvent is variable depending on the purpose of use but is generally in the range of about 10 to about 70 % by weight.

Useful pigments can be inorganic or organic. Inorganic pigments useful in the invention include oxide-type pigments such as titanium dioxide, red iron oxide, chromium oxide and the like; hydroxide-type pigments such as alumina white and the like; sulfate-type pigments such as precipitated barium sulfate and the like; carbonate-type pigments such as precipitated calcium carbonate and the like; silicate-type pigments such as clay and the like; carbon-type pigments such as carbon black and the like.

like; and metallic powders such as aluminium powders, bronze powders, zinc powders and the like. Organic pigments useful in the invention include azo-type pigments such as lake red, first yellow and the like; and phthalocyanine-type pigments such as phthalocyanine blue and the like.

Useful additive resins can be any of cellulose acetate butyrate, bisphenol-type epoxy resins, petroleum resins, phenolic resins, etc. from which a suitable one is selected according to a particular application.

The curable composition of the invention, when required, may contain other additives commonly employed such as surface improvers, cission inhibitors, viscosity modifiers, bubble inhibitors, weatherability improvers (ultraviolet absorbers, light stabilizers, oxidation inhibitors, quenchers and the like), etc. For use, these additives may be simply admixed or chemically bonded to resins, or optionally added such that it is present within the resin particles in the nonaqueous dispersion.

The curable composition of the invention can be easily cured by crosslinking at a low temperature of not higher than 140°C and can accomplish curing, for example, in about 8 hours to about 7 days at room temperature without heating or in about 5 minutes to about 3 hours by heating at about 40 to about 100°C.

The curable composition of the invention is suitable for use as coating compositions, adhesives, inks or the like, and can be provided as coating compositions curable at room temperature and as those of various baking types curable in a wide temperature range from low temperatures of 60 to 100°C to high temperatures of 100 to 160°C. Substrates to be coated with the curable composition of the invention include all kinds of substrates heretofore employed for coating, such as those of iron, plastics, wood or like materials. The curable composition of the invention is particularly suitable for application to automotive body panels or the like.

For use as a topcoating composition, the curable composition of the invention can be formulated into a solid color, metallic color, or clear coating composition and is applied by a wet-on-wet coating method (so-called two-coat one-bake coating), or by a single-layer coating method or the like. The curable composition of the invention can be used to form an intercoating on automotive bodies or a topcoating or undercoating on automotive parts of plastics, metals or the like.

The curable composition of the invention for use as a coating composition can be applied by conventional coating methods without specific limitation, as by air spraying, electrostatic air spraying, airless spraying,

bell electrostatic coating, mini-bell electrostatic coating, roll coating, brushing or the like.

The curable composition of the invention can achieve the following remarkable results.

1. It exhibits an excellent curability at low temperatures.
2. It provides a coating film excellent in resistance to weather and acids and the like.
3. It gives a coating films having an excellent adhesion to various substrates or coating films.
4. It forms a coating film having outstanding appearance properties.

The present invention will be described below in more detail with reference to the following Preparation Examples, Examples and Comparison Examples.

Preparation Example 1

Preparation of Copolymer-1'

$\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{OH}$	30 parts by weight
$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4-$	20 parts by weight
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_4\text{H}_9$	50 parts by weight

The above mixture was subjected to radical polymerization in 100 parts by weight of xylene in the presence of 2,2'-azobisisobutyronitrile (AIBN) at a temperature of 90°C for 3 hours, giving a solution of a copolymer (copolymer-1') having a nonvolatile content of

50% by weight. The copolymer-1' had a number-average molecular weight of 5,000 (as determined by gel permeation chromatography, the measurements shown hereinafter having been obtained by this method).

Preparation of Copolymer-2'

$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_3\text{H}_6\text{Si}(\text{OCH}_3)_3$	20 parts by weight
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_4\text{NCO}$	37 parts by weight
$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$	10 parts by weight
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_4\text{H}_9$	33 parts by weight

The above mixture was reacted under the same conditions as those for preparation of the copolymer-1', giving a solution of a copolymer (copolymer-2') having a nonvolatile content of 50 wt.%. The copolymer-2' had a number-average molecular weight of 6,200.

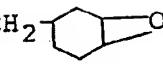
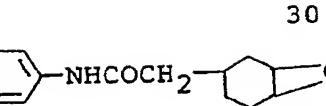
Preparation of Copolymer-3'

$\text{CH}_2=\text{CHCOOH}$	5 parts by weight
$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$	30 parts by weight
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_4\text{H}_9$	65 parts by weight

The above mixture was reacted under the same conditions as those for preparation of the copolymer-1', giving a solution of a copolymer (copolymer-3') having a nonvolatile content of 50 wt.%. The copolymer-3' had a number-average molecular weight of 5,800.

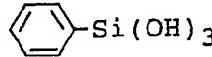
Preparation of Copolymer-1a

$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_4\text{OH}$	10 parts by weight
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$\text{CH}_2=\text{CHCOOCH}_2$ - 	30 parts by weight
$\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{OCONH}-$ 	10 parts by weight
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_3\text{H}_6\text{Si}(\text{OCH}_3)_3$	10 parts by weight
Macromonomer* (described below)	10 parts by weight
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_4\text{H}_9$	30 parts by weight

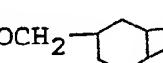
The above mixture was reacted under the same conditions as those for preparation of the copolymer-1', giving a solution of a copolymer (copolymer-1a) having a nonvolatile content of 50 wt.%. The copolymer-1a had a number-average molecular weight of 6,000.

Preparation of Macromonomer*

	7,800 g
$\text{CH}_2=\text{CHCOOC}_3\text{H}_6\text{Si}(\text{OCH}_3)_3$	200 g
Toluene	4,500 g

The above mixture was reacted at 117°C for 3 hours, followed by dehydration. The obtained polysiloxane macromonomer had a number-average molecular weight of 7,000 and contained one vinyl group and 5 to 10 silanol groups on the average per molecule.

Preparation of Copolymer-1b

$\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{OH}$	20 parts by weight
$\text{CH}_2=\text{CHCOOCH}_2$ - 	30 parts by weight
$\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{OCONH}-$ 	10 parts by weight

$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_3\text{H}_6\text{Si}(\text{OCH}_3)_3$	10 parts by weight
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_4\text{H}_9$	30 parts by weight

The above mixture was reacted under the same conditions as those for preparation of the copolymer-1', giving a solution of a copolymer (copolymer-1b) having a nonvolatile content of 50 wt.%. The copolymer-1b had a number-average molecular weight of 6,000.

Preparation of Copolymer-1c

$\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{OH}$	20 parts by weight
$\text{CH}_2=\text{CHCOOCH}_2-\text{Cyclopentane ring with a five-membered epoxide ring attached to one carbon}$	30 parts by weight
$\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{OCONH}-\text{Biphenyl ring}-\text{NHCOCH}_2-\text{Cyclopentane ring with a five-membered epoxide ring attached to one carbon}$	10 parts by weight
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_3\text{H}_6\text{Si}(\text{OCH}_3)_3$	10 parts by weight
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_4\text{H}_9$	10 parts by weight
$\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{C}_8\text{F}_{17}$	20 parts by weight

The above mixture was reacted under the same conditions as those for preparation of the copolymer-1', giving a solution of a copolymer (copolymer-1c) having a nonvolatile content of 50 wt.%. The copolymer-1c had a number-average molecular weight of 7,000.

Preparation of Copolymer-2a

FM-3 monomer**	30 parts by weight
Macromonomer*	30 parts by weight
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_4\text{H}_9$	30 parts by weight
$\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{C}_8\text{F}_{17}$	10 parts by weight

Note: FM-3 monomer** is a trade name for a hydroxyl-containing caprolactone-modified ester of methacrylic acid having an average-molecular weight of 472 and a theoretical hydroxyl value of 119 KOH mg/g, product of Daicel Chemical Co., Ltd.

The above mixture was reacted under the same conditions as those for preparation of the copolymer-1', giving a solution of a copolymer (copolymer-2a) having a nonvolatile content of 50 wt.%. The copolymer-2a had a number-average molecular weight of 5,000.

Preparation of Copolymer-2b

FM-3 monomer**	30 parts by weight
Macromonomer*	30 parts by weight
$\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{C}_8\text{F}_{17}$	40 parts by weight

The above mixture was reacted under the same conditions as those for preparation of the copolymer-1', giving a solution of a copolymer (copolymer-2b) having a nonvolatile content of 50 wt.%. The copolymer-2b had a number-average molecular weight of 4,900.

Preparation of Copolymer-3

$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_4\text{OH}$	15 parts by weight
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}-\text{CH}_2\text{O}'$	40 parts by weight
$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4$	20 parts by weight
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_4\text{H}_9$	25 parts by weight

The above mixture was reacted under the same

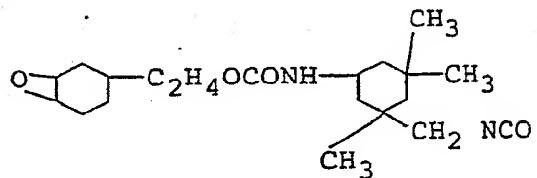
conditions as those for preparation of the copolymer-1', giving a solution of a copolymer (copolymer-3) having a nonvolatile content of 50 wt.%. The copolymer-3 had a number-average molecular weight of 10,500.

Preparation of Copolymer-4

A 400 ml-vol. glass flask equipped with a stirrer was charged with the following ingredients:

Solution of Copolymer-1'
(nonvolatile content 50%) 200 parts by weight

$(CH_3COO)_3SiC_3H_6NCO$ 10 parts by weight

 30 parts by weight

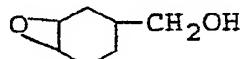
Xylene 40 parts by weight

The mixture was reacted at 100°C for 5 hours with stirring to adduct the hydroxyl group to the isocyanato group. Then it was confirmed that the NCO value reduced to 0.001 or less. The reaction gave a copolymer (copolymer-4) containing groups -OH, $-Si(OCOCH_3)_3$ and .

Preparation of Copolymer-5

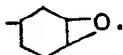
A 400 ml-vol. glass flask equipped with a stirrer was charged with the following ingredients:

Solution of Copolymer-2'
(nonvolatile content 50%) 200 parts by weight

 30 parts by weight

Xylene 30 parts by weight

The mixture was reacted at 100°C for 5 hours with stirring to adduct the hydroxyl group to the isocyanato group. Then it was confirmed that the NCO value reduced to 0.001 or less. The reaction gave a copolymer (copolymer-5) containing groups $-\text{Si}(\text{OCH}_3)_3$ and



Preparation of Copolymer-6

A 400 ml-vol. glass flask equipped with a stirrer was charged with the following ingredients:

Solution of Copolymer-3'
(nonvolatile content 50%) 200 parts by weight

$(\text{CH}_3\text{O})_3\text{SiC}_3\text{H}_6-\text{CH}-\text{CH}_2$ 14.3 parts by weight

Tetraethylammonium bromide 0.1 part by weight

Xylene 14.3 parts by weight

The mixture was reacted at 110°C for 6 hours with stirring to adduct the group $-\text{COOH}$ to the group $-\text{CH}-\text{CH}_2$. Then it was confirmed that the acid value



reduced to 0.01 or lower. The reaction gave a copolymer (copolymer-6) having a group $-\text{Si}(\text{OCH}_3)_3$.

Preparation of Copolymer-7

A glass flask equipped with a stirrer and a water separator was charged with the following ingredients:

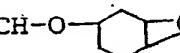
Phthalic anhydride	192 parts by weight
Hexahydrophthalic anhydride	256 parts by weight
Adipic acid	107 parts by weight
Neopentyl glycol	357 parts by weight
Trimethylolpropane	88 parts by weight

The temperature was elevated from 160°C to 230°C over a period of 3 hours. After the temperature was maintained at 230°C for 1 hour, 50 g of xylene was added and the mixture was reacted until the acid value reached 8. The reaction mixture was cooled and diluted with a xylene/n-butanol solvent mixture (4/1, part by weight) to a resin solids concentration of 50% by weight.

The thus obtained copolymer (copolymer-7) was about 3,500 in number-average molecular weight.

Preparation of Copolymer-8

A 400 ml-vol. autoclave of stainless steel equipped with a stirrer was charged with the following ingredients:

CH ₂ =CH-O-C ₄ H ₈ OH	10 parts by weight
CH ₂ =CH-O-C ₂ H ₅	5 parts by weight
CH ₂ =CH-O- 	40 parts by weight

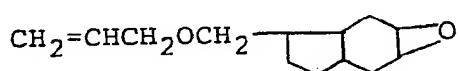
and

Methyl isobutyl ketone	200 parts by weight
2,2'-Azobisisobutyronitrile	.2 parts by weight
Sodium borate	0.5 part by weight

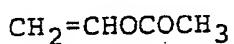
After nitrogen replacement, solidification by cooling and deaeration, 45 parts by weight of a compound $\text{CF}_2=\text{CFCl}$ was placed into the autoclave wherein the temperature was gradually elevated to 60°C. The mixture was reacted with stirring for 16 hours or longer. When the internal pressure in the autoclave was reduced to 1 kg/cm² or lower, the autoclave was cooled with water to terminate the reaction. The obtained resin solution was added to an excess amount of heptane to precipitate the resin. The precipitate was washed and dried, giving 91 g of resin (copolymer-8) in a yield of 91%. The copolymer-8 was 6,300 in number-average molecular weight. The copolymer-8 was dissolved in an equal amount of xylene to obtain a resin solution having a nonvolatile content of 50 wt.%.

Preparation of Copolymer-9

The same procedure as in preparation of the copolymer-8 was repeated with the exception of using the following monomers in place of the monomers for the copolymer-8, giving a solution of a copolymer (copolymer-9) having a nonvolatile content of 50 wt.%. The copolymer-9 had a number-average molecular weight of 7,200.



40 parts by weight



10 parts by weight

$\text{CH}_2=\text{CHOCOC}_3\text{H}_7$	10 parts by weight
$\text{CF}_2=\text{CFCl}$	40 parts by weight

Preparation of Copolymer-10

The same procedure as for preparation of the copolymer-8 was repeated with the exception of using the following monomers in place of the monomers for the copolymer-8, giving a solution of a copolymer (copolymer-10) having a nonvolatile content of 50 wt.%. The copolymer-10 had a number-average molecular weight of 6,800.

$\text{CH}_2=\text{CHSi}(\text{OH})(\text{OCH}_3)_2$	20 parts by weight
$\text{CH}_2=\text{CH-O-}\text{C}_6\text{H}_4\text{O-CH}_2$	10 parts by weight
$\text{CH}_2=\text{CHOC}_2\text{H}_5$	15 parts by weight
$\text{CF}_2=\text{CFCl}$	45 parts by weight
$\text{CF}_2=\text{CF}_2$	10 parts by weight

Preparation of Copolymer-11

The same procedure as for preparation of the copolymer-8 was repeated with the exception of using the following monomers in place of the monomers for the copolymer-8, giving a solution of a copolymer (copolymer-11) having a nonvolatile content of 50 wt.%. The copolymer-11 had a number-average molecular weight of 5,000.

$\text{CH}_2=\text{CHOC}_4\text{H}_8\text{OH}$	15 parts by weight
$\text{CH}_2=\text{CH-O-}\text{C}_6\text{H}_4\text{O-CH}_2$	25 parts by weight

$\text{CH}_2=\text{CHOC}_2\text{H}_5$	5 parts by weight
$\text{CF}_2=\text{CFCl}$	55 parts by weight

Preparation of Copolymer-12

A 400 ml-vol. glass flask equipped with a stirrer was charged with the following ingredients:

Solution of Copolymer-8 (nonvolatile content 50%)	200 parts by weight
$(\text{CH}_3\text{COO})_2\text{Si}-\overset{\text{CH}_3}{\underset{ }{\text{C}_3\text{H}_6}}\text{SH}$	30 parts by weight
Xylene	30 parts by weight

The mixture was reacted with stirring at 96°C for 9 hours. From the disappearance of absorption of -SH group in infrared absorption spectrum, it was confirmed that the reaction gave a copolymer (copolymer-12) having introduced therein a group -OH, epoxy group and a group $-\text{Si}(\text{CH}_3)(\text{OCOCH}_3)_2$. The copolymer-12 had a number-average molecular weight of 8100.

Preparation of Nonaqueous dispersion (1)

A 400 ml-vol. glass flask equipped with a stirrer was charged with the following ingredients:

Solution of Copolymer-4 (nonvolatile content 50%)	200 parts by weight
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_4\text{NCO}$	3.1 parts by weight
Hydroquinone	0.02 part by weight
Xylene	3.1 parts by weight

The mixture was subjected to an addition

reaction with stirring at 100°C for 5 hours. Then it was confirmed that the isocyanate value reduced to 0.001 or less. The thus obtained solution contained a copolymer (dispersion stabilizer (1)) having one polymerizable double bond on the average introduced per molecule.

A glass flask was charged with the following ingredients:

Heptane	95 parts by weight
n-Butyl acetate	5 parts by weight
Solution of dispersion stabilizer (1) (nonvolatile content 50%)	244 parts by weight

The resulting mixture was refluxed with heating. Then the following particle-forming monomers and a polymerization initiator were placed dropwise into the flask over a period of 3 hours, and the mixture was aged for 2 hours.

$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$	10 parts by weight
$\text{CH}_2=\text{CHCN}$	15 parts by weight
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$	20 parts by weight
$\text{CH}_2=\text{CHCOOC}_2\text{H}_4\text{OCONH}-\text{C}_6\text{H}_5-\text{NHCO-CH}_2-\text{C}_5\text{H}_8\text{O}$	30 parts by weight
$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5-\text{C}_3\text{H}_6\text{Si}(\text{CH}_3)_2\text{ON}(\text{CH}_3)_2$	25 parts by weight
2,2'-Azobisisobutyronitrile	1.5 parts by weight

(Particle-forming monomers used totalled 100 parts by weight. Particles/dispersion stabilizer ratio = 45/55, calculated as solids)

The nonaqueous dispersion (1) thus obtained was milky white and stable, had a nonvolatile content of 50 wt.% and contained polymer particles having a mean particle size of 0.15 μm (as determined by Colter-N4, trade name for a product of Colter Co., Ltd.). Neither precipitation nor formation of coarse particles occurred in the dispersion even after the dispersion was left to stand at room temperature for 3 months.

Preparation of Nonaqueous dispersion (2)

A 400 ml-vol. glass flask equipped with a stirrer was charged with the following ingredients:

Solution of copolymer-8 (nonvolatile content 50%)	200 parts by weight
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOH}$	1.6 parts by weight
4-tert-Butylpyrocatechol	0.02 part by weight
Diethylaminoethanol	0.1 part by weight
Xylene	1.6 parts by weight

The mixture was subjected to an addition reaction with stirring at 120°C for 5 hours and it was confirmed that the acid value of the resin reduced to 0.001 mgKOH/g or lower. The reaction gave a solution of a copolymer (dispersion stabilizer (2)) having 0.6 polymerizable double bond on the average introduced per molecule.

A flask was charged with the following ingredients:

Heptane	80 parts by weight
n-Butyl acetate	10 parts by weight
Solution of dispersion stabilizer (2) (nonvolatile content 50%)	200 parts by weight

The mixture was refluxed with heating. The following particle-forming monomers and polymerization initiator were placed dropwise into the flask over a period of 3 hours. Then the mixture was aged for 2 hours and 10 parts by weight of n-butyl acetate was added thereto.

$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5$	10 parts by weight
$\text{CH}_2=\text{CH}-\text{CN}$	10 parts by weight
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$	30 parts by weight
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOC}_2\text{H}_4\text{OH}$	15 parts by weight
$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2-\text{C}_5\text{H}_8\text{O}_2$	30 parts by weight
$\text{CH}_2=\text{CH}-\text{C}_6\text{H}_5-\text{CH}=\text{CH}_2$	5 parts by weight
t-Butylperoxy-2-ethylhexanoate	1.5 parts by weight

(Particle-forming monomers used totalled 100 parts by weight. Particles/dispersion stabilizer ratio = 50/50, calcualted as solids)

The nonaqueous dispersion (2) thus obtained was adjusted with n-butyl acetate to a nonvolatile content of 50% by weight. The nonaqueous dispersion (2) was milky white and stable, and contained polymer particles having a mean particle size of 0.25 μm (as determined by Colter-N4, trade name for a product of Colter Co., Ltd.). Neither

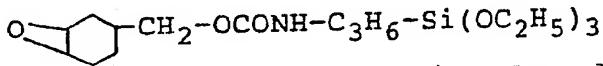
precipitation nor formation of coarse particles occurred even when the dispersion was left to stand at room temperature for 3 months.

Preparation of epoxy- and alkoxy silane-containing compound

A 1 l.-vol. glass flask equipped with a stirrer was charged with the following ingredients:

	128 parts by weight
$\text{OCN-C}_3\text{H}_6-\text{Si}(\text{OC}_2\text{H}_5)_3$	247 parts by weight
Butyl acetate	94 parts by weight

The mixture was reacted at 90°C for 3 hours with stirring, giving a solution of a compound having a nonvolatile content of 80 wt.% and represented by the formula:



Preparation Example 2

Preparation of carboxylic acid compound (C)

Methacrylic acid	10 parts by weight
Styrene	20 parts by weight
n-Butyl methacrylate	60 parts by weight
2-Hydroxyethyl methacrylate	10 parts by weight

The above mixture was subjected to radical polymerization in a solvent mixture of xylene/n-butanol (80/20, part by weight) in the presence of AIBN, giving a solution of a resin (compound (C)) which was 50% by weight in solids content. The compound (C) was 8,000 in number-

average molecular weight and 62 in acid value.

Preparation of carboxylic acid compound (D)

Itaconic acid	15 parts by weight
Styrene	20 parts by weight
n-Butyl acrylate	30 parts by weight
1,4-Butanediol monoacrylate	10 parts by weight
n-Butyl methacrylate	30 parts by weight

The above mixture was subjected to radical polymerization in a solvent mixture of xylene/n-butanol (50/50, part by weight) in the presence of AIBN, giving a solution of a resin (compound (D)) which was 50% by weight in solids content. The compound (D) was 15,500 in number-average molecular weight and 62 in acid value.

Preparation of carboxylic acid compound (E)

Phthalic anhydride	19.5 parts by weight
Adipic acid	19.3 parts by weight
Hexahydropthalic anhydride	20.3 parts by weight
Trimethylol propane	18.0 parts by weight
Neopentyl glycol	32.3 parts by weight

The above mixture was placed into a flask. The temperature was gradually heated to 230°C at which condensation reaction was effected while distilling off the bound water. When the acid value reached 30, the reaction mixture was cooled to 160°C. To the mixture was added 5.4 parts of trimellitic anhydride and the mixture

was maintained at the same temperature for 1 hour and cooled. The mixture was diluted with a solvent mixture of xylene/n-butanol (60/40, part by weight), giving a solution of a resin (compound (E)) having a solids content of 50% by weight. The compound (E) had an acid value of 55 and a number-average molecular weight of 2,800.

Preparation of carboxylic acid compound (F)

A flask was charged with the following ingredients:

Phthalic anhydride	18.0 parts by weight
Hexahydrophthalic anhydride	18.7 parts by weight
Adipic acid	11.8 parts by weight
Trimethylol propane	12.3 parts by weight
Neopentyl glycol	29.8 parts by weight

The temperature was gradually heated to 230°C at which the mixture was subjected to condensation reaction. When the acid value reached 25, the mixture was cooled. Xylene was added to the mixture in such amount as to achieve a concentration of 70% by weight. The resulting mixture was cooled to 100°C and maintained at the same temperature. Thereafter 12.3 parts by weight of hexamethylene diisocyanate was added thereto and the mixture was reacted at 100°C for 1 hour for introduction of urethane linkage. The reaction mixture was diluted with a solvent mixture of xylene/n-butanol (50/50, part by

weight) to produce a solution of a resin (compound (F)) having a solids content of 50% by weight. The compound (F) had a number-average molecular weight of 12,000 and an acid value of 22.

Preparation Example 3

Using the copolymers and nonaqueous dispersions prepared in Preparation Examples given hereinbefore, the curable compositions of the invention containing a carboxylic acid compound as a crosslinking agent were prepared as solid color (white) coating compositions and clear topcoating compositions for use in the two-coat one-bake coating method.

Preparation of solid color (white) coating composition

Table 1 below shows the components and the amounts thereof used for preparing the solid color (white) coating compositions (Nos. S-1 to S-6). In Table 1, the values indicate the amounts in part by weight and the amounts of copolymers and nonaqueous dispersions are shown in terms of part by weight of the resin solids (these definitions are the same in subsequent tables). Titanium dioxide (Titan White CR-95, trade name for a rutile titanium white, product of Isihara Sangyo Kaisha, Ltd.) was used as a white pigment. Before use, titanium dioxide was dispersed in the copolymer solution for 1 hour using a paint shaker. The coating composition No. S-4 was

prepared by dispersing titanium dioxide in the copolymer solution similarly, followed by addition of a nonaqueous dispersion. The amount of the pigment used was 80 parts by weight per 100 parts by weight of the resin solids.

Table 1

<u>Coating comp. No.</u>	<u>S-1</u>	<u>S-2</u>	<u>S-3</u>	<u>S-4</u>	<u>S-5</u>	<u>S-6</u>
Copolymer-2a					40	
" -3			50			
" -5		50				
" -7				25		
" -8		50				
" -12	80					80
Nonaqueous dispersion (2)				50		
Compound A (*1)	20		25	25	40	20
" B (*2)		25				
" C (*3)					20	
Metal chelate compound						
Compound A (*4)	1		0.5	0.5	1	1
" B (*5)		1				
" C (*6)			0.5			
" D (*7)				0.5		

Table 1 (continued)

Coating comp. No.	S-1	S-2	S-3	S-4	S-5	S-6
Carboxylic acid compound						
Compound A (*8)	5					
" B (*9)		10				
" C			10			
" D				10		
" E					20	
" F						10

Preparation of clear coating composition for use in the two-coat one-bake method

Table 2 below shows the components and the amounts thereof used for preparation of clear coating compositions (Nos. M-1 to M-7) useful in the two-coat one-bake method.

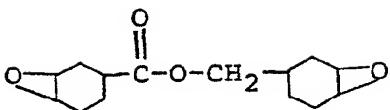
Table 2

<u>Coating comp. No.</u>	<u>M-1</u>	<u>M-2</u>	<u>M-3</u>	<u>M-4</u>	<u>M-5</u>	<u>M-6</u>	<u>M-7</u>
Copolymer-1a	100					20	100
" -2a			40				
" -4					30		
" -6		30					
" -9		50	40	30			
" -10				30			
" -11				30			
Nonaqueous dis- persion							
(1)					50		
(2)						40	
Compound A (*1)		20	20	10	20	20	
" B (*2)						20	
Metal chelate compound							
Compound A (*4)	1		1	0.5	1	1	1
" B (*5)		1					
" C (*6)				0.5			
Carboxylic acid compound							
Compound	(E)	(B)	(A)	(B)	(C)	(F)	(C)
Amount	20	10	10	10	10	10	10

In Tables 1 and 2, the symbols *1 to *9 mean the

following.

(*1) Compound A:



(*2) Compound B:

(*3) Compound C:

(*4) Metal chelate compound A: tris(acetylacetonato) aluminum

(*5) Metal chelate compound B: tris(ethylacetoacetate)aluminum

(*6) Metal chelate compound C: tetrakis(acetylacetonato)zirconium

(*7) Metal chelate compound D: diisopropoxy-bis(ethylacetoacetate)titanium

(*8) Carboxylic acid compound A: trimellitic anhydride

(*9) Carboxylic acid compound B: methyl-hexahydrophthalic anhydride

Examples 1 to 6

The coating compositions S-1 to S-6 were used for Examples 1 to 6, respectively.

Comparison Example 1

The same procedure as in preparation of the coating composition S-6 was repeated with the exception of not using the carboxylic acid compound and gave a coating

composition S-7 for Comparison Example 1.

Comparison Example 2

A coating composition S-8 (Lugabake white, trade name for a coating composition of the polyester/melamine resin type, manufactured by Kansai Paint Co., Ltd.) was used for Comparison Example 2.

Examples 7 to 13

The coating compositions M-1 to M-7 were used for Examples 7 to 13, respectively.

Comparison Example 3

The same procedure as in preparation of the coating composition M-7 was repeated with the exception of not using the carboxylic acid compound and gave a coating composition M-8 for Comparison Example 3.

Comparison Example 4

A coating composition M-9 (Magicron #1000 Clear, trade name for a coating composition of the acryl/melamine resin type, manufactured by Kansai Paint Co., Ltd.) was used for Comparison Example 4.

Preparation of base coating composition A

A base coating composition for use in wet-on-wet coating was prepared from the following ingredients:

Copolymer-1a (solution)	200 parts by weight
Tris(acetylacetonato)aluminum	2 parts by weight
EAB-551-02 (trade name for cellulose acetate butylate, pro-	

duct of Eastman Kodak Co.)	20 parts by weight
Toluene	30 parts by weight
Butyl acetate	30 parts by weight
Aluminum paste #4919 (trade name for a product of Toyo Aluminum Co., Ltd.)	5 parts by weight
Aluminum paste #55-519 (trade name for a product of Toyo Aluminum Co., Ltd.)	10 parts by weight

The obtained composition was adjusted to a viscosity of 15 seconds (Ford cup #4, 25°C) with a solvent mixture of toluene/xylene/n-butanol (40/40/20) before application.

Production of substrate to be coated

Substrates to be coated with coating compositions were produced as follows.

To a dull-finished steel panel treated by zinc phosphate was applied an epoxy resin-type cationic electrodeposition coating composition to a film thickness of about 25 μm and cured by heating at 170°C for 30 minutes. Lugabake AM (trade name for a product of Kansai Paint Co., Ltd.) as an intercoating composition was applied to the primed panel to a dry film thickness of about 30 μm and the coated panel was baked at 140°C for 30 minutes. The coating surface was subjected to wet-grinding with #400 sandpaper, dried and wiped with a piece of cloth saturated with petroleum benzine to give a

substrate panel.

[Test for properties of coating film]

Solid color coating composition

The coating compositions obtained in Examples 1 to 6 and Comparison Examples 1 and 2 were adjusted to a viscosity of 22 seconds (Ford cup No. 4, 20°C) with Swasol #1000 (trade name for a product of Cosmo Oil Co., Ltd., petroleum type solvent). Each composition was applied to the substrate panel to a dry film thickness of 40 to 50 μm , set at room temperature for 10 minutes and baked at 120°C for 30 minutes (the substrate panels coated with the coating compositions for Comparison Examples were baked at 140°C for 30 minutes) to produce test coated panels. The test coated panels were tested for properties. Table 3 shows the test results.

Table 3

	Example						Comp. Example	
	1	2	3	4	5	6	1	2
Coating composition	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8
State of coating surface (*11)	A	A	A	A	A	A	A	A
Gloss (60°)	91	92	94	93	92	90	92	92
Pencil hardness	H	H	F	H	H	F	B	F
Water resistance (*12)	A	A	A	A	A	A	A	B
Acid resistance (*13)	A	A	A	A	A	A	A	C
Impact resistance (*14)	40	40	40	40	40	40	30	30
Adhesion-1 (*15)	100/100	100/100	100/100	100/100	100/100	100/100	50/100	0/100
Adhesion-2 (*16)	100/100	100/100	100/100	100/100	100/100	100/100	10/100	0/100
Weatherability (*17)	A	A	A	A	A	A	A	C

Clear coating composition for use in the two-coat one-bake method

The base coating composition A was applied to substrate panels. In about 5 minutes the coated substrate panels were coated with each of the coating compositions for Examples 7 to 13 and Comparison Examples 3 and 4 diluted with Swasol #1000 to a viscosity of 22 seconds. The dry thickness of films of the base coating composition was 15 to 20 μm and that of films of the clear coating composition was 35 to 45 μm . Then the coated substrate panels were left to stand at room temperature for about 10 minutes and baked at 120°C for 30 minutes (the substrates coated with the compositions for Comparison Examples were baked at 140°C for 30 minutes), producing test coated panels. The test coated panels were tested for properties. Table 4 shows the test results.

Table 4

	Example						
	7	8	9	10	11	12	13
Coating composition	M-1	M-2	M-3	M-4	M-5	M-6	M-7
State of coating surface (*11)	A	A	A	A	A	A	A
Gloss (60°)	91	93	92	93	94	92	92
Pencil hardness	F	F	F	F	F	F	F
Water resistance (*12)	A	A	A	A	A	A	A
Acid resistance (*13)	A	A	A	A	A	A	A
Impact resistance (*14)	35	35	40	35	40	40	40
Adhesion-3 (*18)	100/100	100/100	100/100	100/100	100/100	100/100	100/100
Weatherability (*17)	A	A	A	A	A	A	A

Table 4 (continued)

	Comparison Example	
	3	4
Coating composition	M-8	M-9
State of coating surface (*11)	A	B
Gloss (60°)	93	92
Pencil hardness	B	F
Water resistance (*12)	A	B
Acid resistance (*13)	A	C
Impact resistance (*14)	30	25
Adhesion-3 (*18)	20/100	10/100
Weatherability (*17)	A	C

In Tables 3 and 4, the symbols *11 to *18 indicate the following.

(*11) State of coating surface

The test coated panels were observed with the unaided eye to evaluate the appearance according to the following criteria:

A: Excellent

B: Slightly unsatisfactory in surface smoothness

C: Poor in surface smoothness

(*12) Water resistance

The test coated panel was immersed in a thermo-static water bath at 40°C for 240 hours. After withdrawal, the water resistance of the test coated panel was evaluated in terms of loss of gloss, blistering and like change according to the following ratings:

A: No change.

B: Slight loss of gloss caused

C: Loss of gloss and blistering caused

(*13) Acid resistance

The test coated panel was immersed in 40% by weight H_2SO_4 at 40°C for 5 hours, withdrawn and washed with water after which the acid resistance was evaluated according to the following criteria:

A: No change

B: Slight loss of gloss caused

C: Loss of gloss and blistering caused

(*14) Impact resistance

The impact resistance of the test coated panel was determined using a Du Pont impact tester (1/2 inch diameter of impact load element, 0.5 kg weight). The impact resistance was assessed in terms of the maximum height (cm) at which the dropping of the weight caused no cracking on the coating surface.

(*15) Adhesion-1

Panels of polished mild steel were used as sub-

strates to be coated. After degreasing, the mild steel panel was coated with the coating composition by spraying and baked at 120°C for 30 minutes. Then the coated panel was immersed in hot water at 80°C for 5 hours, withdrawn, and dried at room temperature for 1 hour. The surface of the coated panel was cut crosswise to the substrate at a spacing of 1 mm to form 100 squares. Cellophane adhesive tape was applied over the cut surface and removed. The adhesion was evaluated in terms of a value given by:

(the number of squares remaining adhered)/100.

(*16) Adhesion-2

Test coated panels were produced in the same manner as those prepared for testing the solid color coating compositions. The obtained test coated panel was further baked at 140°C for 30 minutes, thereafter coated with the same solid color coating composition to a dry film thickness of 40 μm and baked at 120°C for 30 minutes. The test coated panels were immersed in hot water at 80°C for 5 hours, dried at room temperature for 1 hour and subjected to the same cross-cut test as above in Adhesion-1.

(*17) Weatherability

Using an accelerated weathering tester (manufactured by Q Panel Co., Ltd.), a QUV accelerated exposure test was carried out under conditions of one

cycle comprising:

UV irradiation 16 hr/60°C

water condensation 8 hr/50°C

After conducting 125 cycles (3000 hours), the weatherability was evaluated according to the following ratings.

- A: Retaining substantially the same gloss as in initial stage.
- B: Slightly reduced in gloss but free of cracking, blushing and the like.
- C: Significantly reduced in gloss and marked in cracking and chalking.

(*18) Adhesion-3

Substrate panels were prepared in the same manner as done for the clear coating compositions useful for the two-coat one-bake method and further baked at 140°C for 30 minutes. The base coating composition and the clear top coating composition of the types as used above were applied to the substrate panels in the same manner and the coated panels were baked at 120°C for 30 minutes. The coated panels were thereafter immersed in hot water at 80°C for 5 hours, withdrawn from the hot water and dried at room temperature for 1 hour. Then the same cross-cut adhesion test as above was conducted.

Preparation Example 4

Using the copolymers and nonaqueous dispersions prepared in Preparation Examples given hereinbefore, the curable compositions of the invention containing a polyisocyanate compound as a crosslinking agent were prepared as solid color coating compositions (white) and clear top coating compositions for the two-coat and one-bake method.

Preparation of solid color coating composition (white)

Table 5 below shows the components and amounts thereof for preparing solid color (white) coating compositions (coating compositions Nos. S-9 to S-14). Titanium dioxide was used as a white pigment as in Preparation Example 3.

Table 5

<u>Component</u>	<u>-2a</u>	<u>Coating composition No.</u>					
		<u>S-9</u>	<u>S-10</u>	<u>S-11</u>	<u>S-12</u>	<u>S-13</u>	<u>S-14</u>
Copolymer						40	
"	-3			50			
"	-5		50				
"	-7				25		
"	-8		50				
"	-12	80					80
<u>Nonaqueous dispersion (2)</u>				50			
Compound	A (*1)	20		25	25	40	20
"	B (*2)		25				
"	C (*3)					20	
<u>Metal chelate compound</u>							
Compound	A (*4)	1		1	0.5	1	1
"	B (*5)		1				
"	C (*6)			0.5			
"	D (*7)				0.5		
<u>SUMIDUL N (*19)</u>		5	5	7.5	5	10	
<u>TAKENATE B-815N (*20)</u>							10
<u>Dibutyltin dilaurate</u>							0.1

Preparation of clear coating composition for use in the
two-coat one-bake method

Table 6 below shows the components and amounts thereof for preparing clear coating compositions useful for the two-coat one-bake method (coating compositions Nos. M-10 to M-16).

Table 6

Component	-lb	Coating composition No.					
		M-10	M-11	M-12	M-13	M-14	M-15
Copolymer		100				20	100
"	-2a			40			
"	-4					30	
"	-6		30				
"	-9		50	40	30		
"	-10				30		
"	-11				30		
Nonaqueous dispersion (1)						50	
"	(2)					40	
Compound	A (*1)		20	20	10	20	20
"	B (*2)					20	
"	C (*3)						
Metal chelate compound							
Compound	A (*4)	1		1	0.5	1	1
"	B (*5)		1				
"	C (*6)				0.5		
SUMIDUL N (*19)		10	5	10	5	10	5
TAKENATE B-815N (*20)							10
Dibutyltin dilaurate							0.1

The symbols *1 to *7 are as described above.

The symbols *19 to *20 mean the following.

(*19) SUMIDUL N: product of Sumitomo Bayer Urethane Co., Ltd., biuret type polyisocyanate (active ingredient 75 wt.%, NCO content 16.5 wt.%)

(*20) TAKENATE B-815N: product of Takeda Chemical Industries, Ltd.
Non-yellowing type blocked polyisocyanate

Examples 14 to 19

The coating compositions S-9 to S-14 were used for Examples 14 to 19, respectively.

Comparison Example 5

The coating composition S-15 identical with the coating composition S-14 but free of TAKENATE B-815N and dibutyltin dilaurate was used for Comparison Example 5.

Examples 20 to 26

The coating compositions M-10 to M-16 were used for Examples 20 to 26, respectively.

Comparison Example 6

The coating composition M-17 identical with the coating composition M-16 but free of TAKENATE B-815N and dibutyltin dilaurate was used for Comparison Example 6.

Comparison Example 7

The coating composition M-18 (tradename, Magicron #1000 Clear, product of Kansai Paint Co., Ltd.,

acryl/melamine resin-type coating composition) was used for Comparison Example 7.

Preparation of base coating composition B

Using azobisisobutyronitrile as a polymerization initiator, the following monomer mixture was subjected to radical polymerization in a solvent mixture of xylene/n-butanol (80/20, part by weight), giving a solution of vinyl copolymer. The vinyl copolymer had a number-average molecular weight of 18,000. The vinyl copolymer solution had a nonvolatile content of 50% by weight and a viscosity of Z1 (as determined by Gardner-Holdt bubble viscometer).

Methyl methacrylate 40 parts by weight

Ethyl acrylate 20 parts by weight

n-Butyl acrylate 20 parts by weight

2-Hydroxyethyl methacrylate 18 parts by weight

Acrylic acid 2 parts by weight

A base coating composition B for wet-on-wet coating was prepared from the following components.

Vinyl copolymer solution obtained above (nonvolatile content 50 wt.%) 160 parts by weight

U-Van 28SE-60 (tradename, Mitsui Toatsu Chemicals Inc., melamine resin, nonvolatile content 60 wt.%) 33.3 parts by weight

EAB-551-2 (tradename, Eastman Kodak Co., cellulose acetate butyrate) 20 parts by weight

Toluene	30 parts by weight
Butyl acetate	30 parts by weight
Aluminum paste #4919 (tradename for product of Toyo Aluminum Co., Ltd.)	5 parts by weight
Aluminum paste #55-519 (tradename for product of Toyo Aluminum Co., Ltd.)	5 parts by weight

Using a solvent mixture of toluene/xylene/n-butanol (40/40/20, part by weight), the coating compositions were adjusted to a viscosity of 15 seconds (Ford Cup No.4/25°C).

Production of substrate to be coated

A dull finished steel panel treated by zinc phosphate was further treated in the same manner as above to give a substrate panel.

[Test for properties of coating film]

Solid color coating composition

The coating compositions prepared in Examples 14 to 19 and Comparison Example 5 were adjusted to the same viscosity as above and applied to substrate panels, and the coated substrate panels were similarly set and baked to give test coated panels. The test coated panels were tested for properties. Table 7 shows the test results.

Table 7

	Example						Comparison
	14	15	16	17	18	19	Example
Coating composition	S-9	S-10	S-11	S-12	S-13	S-14	S-15
State of coating surface (*11)	A	A	A	A	A	A	A
Gloss (60°)	90	91	94	94	92	91	90
Pencil hardness	H	H	H	H	2H	F	F
Water resistance (*12)	A	A	A	A	A	A	B
Acid resistance (*13)	A	A	A	A	A	A	B
Impact resistance (*14)	50<	50<	50<	50	45	45	35
Weatherability (*17)	A	A	A	A	A	A	A

Clear coating composition for use in the two-coat one-bake method

The base coating composition B was applied to the surface of substrate panels and the coated panels were allowed to stand for 5 minutes. Thereupon the coating compositions of Examples 20 to 26 and Comparison Examples 6 and 7 diluted to a viscosity of 22 seconds with Swasol #1000 (tradename for product of Cosmo Oil Co., Ltd.) were applied to the coated substrate panels and the coated panels were allowed to stand and baked in the same manner as above to give test coated panels. The test coated panels were tested for properties. Table 8 shows the test

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results.

Table 8

Coating composition	State of coating surface (*11)	Example						Comp. Example	
		20	21	22	23	24	25	26	6
	M-10	20	21	22	23	24	25	26	7
	M-11								
	M-12								
	M-13								
	M-14								
	M-15								
	M-16								
	M-17								
	M-18								
Gloss (60°)		95	93	96	91	94	94	94	94
Pencil hardness		H	H	H	H	2H	H	H	H
Water resistance (*12)		A	A	A	A	A	A	B	A
Acid resistance (*13)		A	A	A	A	A	A	B	C
Impact resistance (*14)		50<	50	50<	50	50<	45	45	35
Weatherability (*17)		A	A	A	A	A	A	A	C
Adhesion-4 (*21)		100/100	100/100	100/100	100/100	100/100	100/100	25/100	0/100

The symbols *11 to *14 and *17 are as described above. *21 "Adhesion-4" means the following.

(*21) Adhesion-4

Urethane resin panels cut from an automotive bumper made of urethane resin were degreased with trichloroethane vapor. The coating compositions were applied to the degreased panels to a dry thickness of about 40 μm and the coated panels were baked at 120°C for 30 minutes. The coated panels were immersed in warm water at 40°C for 5 days, withdrawn from the warm water and dried for 2 hours. A lattice pattern with eleven cuts in each direction was made in the coating film to the substrate to form 100 squares (1 mm^2). Cellophane tape was applied over the lattice and then removed, and the adhesion was evaluated in terms of a value given by: (the number of squares remaining adhered)/ 100.

Preparation Example 5

Using the copolymers and nonaqueous dispersions obtained in Preparation Examples given above, the curable compositions of the invention containing an aminoaldehyde resin as a crosslinking agent were prepared as solid color coating compositions (white) and clear top coating compositions for use in the two-coat and one-bake method.

Preparation of solid color (white) coating composition

Table 9 shows the components and amounts thereof

for preparing solid color coating compositions (white) (coating composition Nos. S-16 to S-21). Titanium dioxide was used as a white pigment as done in Preparation Example 3.

Table 9

<u>Component</u>	<u>Coating composition No.</u>					
	<u>S-16</u>	<u>S-17</u>	<u>S-18</u>	<u>S-19</u>	<u>S-20</u>	<u>S-21</u>
<u>Copolymer -2b</u>					40	
" -3			50			
" -5		50				
" -7				25		
" -8		50				
" -12	80					80
<u>Nonaqueous dispersion (2)</u>				50		
<u>Compound A (*1)</u>	20		25	25	40	20
<u>Compound B (*2)</u>			25			
<u>Compound C (*3)</u>					20	
<u>Metal chelate compound</u>						
<u>Compound A (*4)</u>	1		0.5	0.5	1	1
" B (*5)		1				
" C (*6)			0.5			
" D (*7)				0.5		
<u>CYMEL 235 (*22)</u>	10	5	5	5	15	
<u>U-Van 28SE (*23)</u>						10
<u>Acid catalyst (*24)</u>	0.5	0.2	0.2	0.2	0.5	

Preparation of clear coating composition for use in the
two-coat one-bake method

Table 10 shows the components and amounts thereof for preparing clear coating compositions for use in the two-coat one-bake method (coating compositions Nos. M-19 to M-25).

Table 10

<u>Component</u>	<u>Coating composition No.</u>						
	<u>M-19</u>	<u>M-20</u>	<u>M-21</u>	<u>M-22</u>	<u>M-23</u>	<u>M-24</u>	<u>M-25</u>
Copolymer -1c	100					20	100
" -2b		40					
" -4					30		
" -6		30					
" -9		50	40	30			
" -10				30			
" -11				30			
Nonaqueous dispersion							
(1)					50		
(2)						40	
Compound A (*1)		20	20	10	20	20	
" B (*2)						20	
" C (*3)							
Metal chelate compound							
Compound A (*4)	1		1	0.5	1	1	1
" B (*5)		1					
" C (*6)				0.5			
" D (*7)							
CYMEL 235 (*22)	10	5	10	5	10	5	
U-Van 28SE (*23)							10
Acid catalyst (*24)	0.5	0.2	0.5	0.2	0.5	0.2	

The symbols *1 to *7 are as described above.

The symbols *22 to *24 indicate the following.

(*22) CYMEL 235: tradename, Mitsui Cyanamido Co., Ltd., methyl/n-butyl etherified monomeric melamine resin

(*23) U-Van 28SE: tradename, Mitsui Toatsu Chemicals Inc., n-butyl alcohol-modified melamine resin (nonvolatile content 60 wt. %)

(*24) Acid catalyst: dodecylbenzenesulfonic acid neutralized with dimethyl ethanolamine (to 1.0 equivalent)

Examples 27 to 32

The coating compositions S-16 to S-21 were used for Examples 27 to 32, respectively.

Comparison Example 8

The coating composition S-22 identical with the coating composition S-21 but free of U-Van 28SE was used for Comparison Example 8.

Examples 33 to 39

The coating compositions M-19 to M-25 were used for Examples 33 to 39, respectively.

Comparison Example 9

The coating composition M-26 identical with the coating composition M-25 but free of U-Van 28SE was used for Comparison Example 9.

Preparation of substrate to be coated

A dull finished steel panel treated by zinc

phosphate was further treated in the same manner as above to give a substrate panel.

[Test for properties of coating film]

Solid color coating composition

The coating compositions prepared in Examples 27 to 32 and Comparison Examples 8 were adjusted to the same viscosity as above and applied to substrate panels. The coated substrate panels were similarly set and baked to give test coated panels. The test coated panel were tested for properties. Table 11 shows the test results.

Table 11

	Example						Comp. Example
	27	28	29	30	31	32	8
Coating composition	S-16	S-17	S-18	S-19	S-20	S-21	S-22
State of coating surface (*11)	A	A	A	A	A	A	A
Gloss (60°)	90	91	94	94	92	91	90
Pencil hardness	H	H	H	H	2H	F	B
Water resistance (*12)	A	A	A	A	A	A	B
Acid resistance (*13)	A	A	A	A	A	A	A
Impact resistance (*14)	40	40	40	50	40	40	20
Adhesion - 5 (*25)	100/100	100/100	100/100	100/100	100/100	100/100	100/100
Adhesion - 6 (*26)	100/100	100/100	100/100	100/100	100/100	100/100	10/100
Weatherability (*17)	A	A	A	A	A	A	A

Clear coating composition for use in the two-coat one-bake method

The base coating composition B was applied to substrate panels and the coated panels were allowed to stand for 5 minutes. Thereupon the coating compositions of Examples 33 to 39 and Comparison Example 9 diluted to a viscosity of 22 seconds with Swasol #1000 were applied to coated panels. The coated panels were allowed to stand and baked in the same manner as above to give test coated panels. The test coated panels were tested for properties. Table 12 shows the test results.

Table 12

	Example						Comp. Example	
	33	34	35	36	37	38	39	9
Coating composition	M-19	M-20	M-21	M-22	M-23	M-24	M-25	M-26
State of coating surface	A	A	A	A	A	A	A	A
(*11)								
Gloss (60°)	95	93	96	91	94	94	94	93
Pencil hardness	H	H	H	H	2H	H		B
Water resistance (*12)	A	A	A	A	A	A		B
Acid resistance (*13)	A	A	A	A	A	A		A
Impact resistance (*14)	35	35	35	35	50	45	35	20
Weatherability (*17)	A	A	A	A	A	A	A	A
Distinctness-of-image gloss -1 (*27)	88	89	91	92	91	87	87	68
Distinctness-of-image gloss -2 (*28)	0.9	0.9	0.9	0.9	0.9	0.9	0.9	0.3

The symbols *11 to *14 and *17 are as described above. The symbols *25 to *28 indicate the following.

(*25) Adhesion-5

A substrate coated with Lugabake AM (tradename, Kansai Paint Co., Ltd., polyester resin/melamine resin baking-type coating composition) was baked at 140°C for 30 minutes and further baked at 160°C for 30 minutes. Such treated substrates were used in preparing substrate panels.

A lattice pattern with eleven cuts in each direction was made in the coating film to the substrate to form 100 squares (1 mm²). Cellophane adhesive tape was applied over the lattice and then removed, and the adhesion was evaluated in terms of a value given by: (the number of squares remaining adhered)/100.

(*26) Adhesion-6

A test coated panel prepared by the same method as in Adhesion-5 was immersed in hot water at 60°C for 3 days, withdrawn from the hot water and dried for 1 hour. The same cross-cut adhesion test as in adhesion-5 was carried out. The values in the table indicate the same evaluation as in Adhesion-5.

(*27) Distinctness-of-image gloss -1

The distinctness-of-image gloss was measured with an image clarity meter (manufactured by Suga Tester

Co., Ltd.). The values in the table represent ICM values which vary from 0 to 100%. The larger the ICM value, the higher the distinctness-of-image gloss. The ICM value not less than 80 represents a high distinctness-of-image gloss.

(*28) Distinctness-of-image gloss -2

The distinctness-of-image gloss was measured with a Gd meter for measuring the distinctness-of-image gloss (JCRI-GGD-166 model manufactured by Nippon Shikisai Kenkyusho) at a fixed angle of 55°.

CLAIMS:

1. A curable composition comprising:

(I) a resin component containing as essential functional groups epoxy group, and silanol group and/or hydrolyzable group directly attached to silicon atom,
(II) at least one crosslinking agent selected from the group consisting of carboxylic acid compounds, polyisocyanate compounds and aminoaldehyde resins, and
(III) at least one curing catalyst selected from the group consisting of organometallic compounds, Lewis acids, protonic acids and compounds having Si-O-Al bond or bonds.

2. A curable composition according to claim 1 wherein (I) resin component further contains hydroxyl group as essential functional group.

3. A curable composition according to claim 1 wherein the epoxy group contained in (I) resin component is alicyclic.

4. A curable composition according to claim 1 wherein (I) resin component is used as dissolved or dispersed in a solvent or in the form of a nonaqueous dispersion of polymer particles prepared in the presence of said resin component as a dispersion stabilizer.

5. A curable composition according to claim 1 wherein (II) crosslinking agent is a carboxylic acid compound and is used in an amount of about 1 to about 40

parts by weight per 100 parts by weight of (I) resin component, calculated as solids.

6. A curable composition according to claim 1 wherein (II) crosslinking agent is a polyisocyanate compound and is used in an amount of about 1 to about 30 parts by weight per 100 parts by weight of (I) resin component, calculated as solids.

7. A curable composition according to claim 1 wherein (II) crosslinking agent is an aminoaldehyde resin and is used in an amount of about 1 to about 50 parts by weight per 100 parts by weight of (I) resin component, calculated as solids.

8. A curable composition according to claim 1 wherein (III) curing catalyst is at least one organometallic compound selected from the group consisting of metal alkoxide compounds, metal chelate compounds and metal alkyl compounds.

9. A curable composition according to claim 8 wherein (III) curing catalyst is a metal chelate compound.

10. A curable composition according to claim 1 wherein (III) curing catalyst is at least one compound selected from organometallic compounds, Lewis acids and protonic acids, and is used in an amount of about 0.01 to about 30 parts by weight per 100 parts by weight of combined amount of (I) resin component and (II)

crosslinking agent, calculated as solids.

11. A curable composition according to claim 1 wherein (III) curing catalyst is a compound having Si-O-Al bond or bonds and is used in an amount of about 1 to about 100 parts by weight per 100 parts by weight of combined amount of (I) resin component and (II) crosslinking agent, calculated as solids.